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To the Graduate Council:

I am submitting herewith a thesis written by Charles Phillip Rader entitled "Competitive Catalytic Hydrogenation of Benzene, Toluene, and the Polymethylbenzenes on Platinum." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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COMPETITIVE CATALYTIC HYDROGENATION OF BENZENE, TOLUENE, AND
THE POLYMETHYLENZES ON PLATINUM

A Thesis
Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Charles Phillip Rader

August 1961

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TO

CLARITA ANNE

AND

CLARITA MARIE

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CHAPTER I

INTRODUCTION

A. Purpose of This Research

This investigation embraced a comparison of the relative rates of hydrogenation on platinum of benzene and several of its methyl-substituted derivatives with their relative strengths of adsorption on the active spots of the catalyst surface. It consisted of the determination of the rate of reduction of the individual hydrocarbons and a variety of their binary mixtures. Its ultimate goal was to aid in the elucidation of the mechanism by which the benzene nucleus accepts hydrogen on a platinum surface.

B. Historical Background

The catalytic hydrogenation of the benzene nucleus epitomizes the tremendous progress which has been made in the field of surface catalysis during the past sixty years. The practical and theoretical importance of this reaction is exceeded only by its complexity. Its complexity attests to the vast amount of theoretical and experimental investigation which is yet to be carried out if the phenomenon of heterogeneous catalysis is to be adequately understood.

In 1901 Sabatier and Senderens¹ reported the first successful reduction of the benzene nucleus on a catalyst surface. They hydrogenated benzene and several of its homologs over a nickel catalyst

at atmospheric pressure and temperatures of 70-200°. The benzene ring was found to be completely reduced to a cyclohexane ring. Later investigations of these workers² revealed that the benzene ring could be reduced with various functional groups attached to it. This work has been summarized by Sabatier.³

In a series of systematic researches Ipatieff developed a method by which benzene and many of its derivatives could be conveniently reduced at temperatures of 150-300° and pressures of 50-220 atmospheres over a nickel or nickel oxide catalyst. Since the reductions were carried out in the liquid phase with agitation, Ipatieff was able to disprove a previously-held theory that reactions on a solid surface could take place only when the solid was in contact with the gaseous phase. Ipatieff has conveniently summarized all of his earlier works on aromatic hydrogenation.⁴

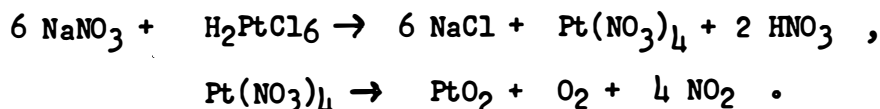
Willstatter^{5,6} discovered that benzene and its derivatives could be reduced to the corresponding cyclohexanes over platinum black and colloidal platinum at room temperature and atmospheric pressure. Reductions were carried out in ether, acetic acid, or in the absence of solvent. Benzene was hydrogenated over colloidal platinum in aqueous gum arabic by Skita and Meyer.⁷ Several polymethylbenzenes were reduced over the same catalyst in acetic acid by Skita and Schneck.⁸ Platinum had previously been regarded by Sabatier and Senderens¹ as unsuitable for the reduction of benzene in the gaseous phase.

Other early investigations resulted in the development of new catalysts for aromatic hydrogenation. Zelinsky and Komarewsky⁹ found that a superior nickel catalyst resulted from the deposition of the

metal on either activated alumina or charcoal. Adkins¹⁰ carried out a comprehensive study of the reduction of the benzene ring on nickel and copper-chromium oxide catalysts. Lommel and Goost¹¹ were successful in reducing aniline to cyclohexylamine over a cobalt catalyst at 100 atmospheres hydrogen pressure.

The most useful catalysts to emerge from the early investigations of aromatic hydrogenation were Raney nickel¹² and Adams platinum oxide.¹³ Raney nickel is prepared by the action of sodium hydroxide upon a nickel-aluminum alloy. The aluminum is dissolved leaving a highly active nickel catalyst. Numerous investigations have been carried out to ascertain the specific nature of this catalyst.¹⁴ Unfortunately, the specific action of Raney nickel is still not clearly understood. Raney nickel catalyzes the hydrogenation of the benzene nucleus only at elevated temperatures and pressures.

Adams platinum, on the other hand, facilitates the reduction of benzene at room temperature and atmospheric pressure. This catalyst is prepared by the fusion of sodium nitrate with chloroplatinic acid. The reactions taking place are,



The platinum dioxide is reduced in situ to the active catalyst. Adams and Voorhees¹⁵ have concluded that the active catalyst is either a lower oxide or hydroxide of platinum. This conclusion is corroborated by an earlier report by Willstatter and Waldschmidt-Leitz¹⁶ of the necessity of oxygen on the surface of platinum black for the reduction of the benzene ring. Adams platinum oxide is most commonly used with an acidic solvent.

Comprehensive reviews of the earlier works on aromatic hydrogenation have been written by Smith,¹⁷ Ellis,¹⁸ and Berkman, Morrell, and Egloff.¹⁹ It should be noticed that virtually all of the hydrogenation studies of the benzene ring prior to 1930 were mainly concerned with the discovery and development of new methods of synthesis since the reaction affords a convenient synthetic route to many compounds possessing a cyclohexane ring. Thus, much of the early knowledge of the reduction of the benzene nucleus consisted of reactions which would proceed favorably on a specific catalyst under a given set of experimental conditions. Some concerted attempts were made, however, to explain how the ring could accept hydrogen on a solid surface.¹⁶ It slowly became apparent that the reaction could be adequately explained only with the aid of knowledge of a more fundamental nature. This knowledge was forthcoming from the work of Langmuir, Taylor, Hinshelwood, and others.

C. Nature of Hydrogenation Catalysts

The immense complexity of heterogeneous catalysis may be attributed to the meagerly understood participation of the catalyst surface. This is in contrast to homogeneous reactions where the structure and energy content of all reaction participants are known to a much higher degree of confidence. Thus, it is not surprising that the progress toward a more fundamental understanding of surface catalysis has been greatly dependent upon the elucidation of the nature and properties of the catalyst. Catalytic hydrogenation is an excellent example of this fact.

In 1916 Langmuir²⁰ put forward the idea that surface reactions take place as a result of the valency forces which the surface exerts upon one or more reactants. The valency forces are of the same nature as those which exist in ordinary chemical bonds since they arise from the quantum-mechanical pairing of electrons or from electrostatic attraction. Thus, when benzene is reduced with hydrogen, it is necessary that either one or both reactants becomes chemically bonded to the surface prior to undergoing reaction.

The idea of intermediate compound formation suggests an intimate relationship between heterogeneous catalysis and chemisorption. Such a relationship has received sound theoretical and experimental justification. The complexity and importance of chemisorption rival those of surface catalysis itself. Authoritative reviews of chemisorption and its relationship to catalysis have been written by Laidler,²¹ Trapnell,²² Kwan,²³ and de Boer.²⁴

It is well known that the best hydrogenation catalysts for the benzene nucleus are the transition metals of group VIII in the periodic table and certain oxides and sulfides of the group VIb and group VIII elements. The activity of these catalysts must, therefore, depend upon their ability to form quasi-stable bonds with hydrogen and/or the benzene ring. It is extremely difficult to ascertain the specific properties of the quasi-stable compounds formed on the catalyst surface. There is good reason to believe that they vary greatly from catalyst to catalyst and even from region to region of the same catalyst.^{25,26} It can be stated with assurance, however, that the formation of the

intermediate compound lowers the potential energy barrier (activation energy) which the reactants must surmount if they are to undergo reaction. This lowering of the activation energy will accelerate the rate of reaction.

The potential energy barriers over which the reactants must pass are depicted in Figure 1. Point A on Figure 1 represents the potential energy of the reactants prior to adsorption on the catalyst surface. At point B the reactant molecules are in an activated state leading to chemisorption. Point C signifies the energy level when either one or both reactants are chemisorbed on the surface. The zenith of the energy level is usually reached at D which corresponds to the energy level of the activated complex (transition state) of the surface reaction. From D the energy of the system decreases to E which represents the energy level of the adsorbed product. Desorption of product corresponds to passage through another activated complex at F and thence to G which signifies the energy level of the product.

It should be noted that vertical distances AG and AC represent the heats of reaction and adsorption respectively. Distance AB is the activation energy for chemisorption of reactants, and CD is the true activation energy of the surface reaction. The relative heights of points B, D, and F will determine which reaction step determines the overall rate of reaction. The slow or rate-determining step will have the highest energy barrier. If point D corresponds to the slow step, the reaction rate will decrease as the strength of the catalyst-reactant bonds increases. Beeck²⁷ has demonstrated this to be the case for the hydrogenation of ethylene on metals films.

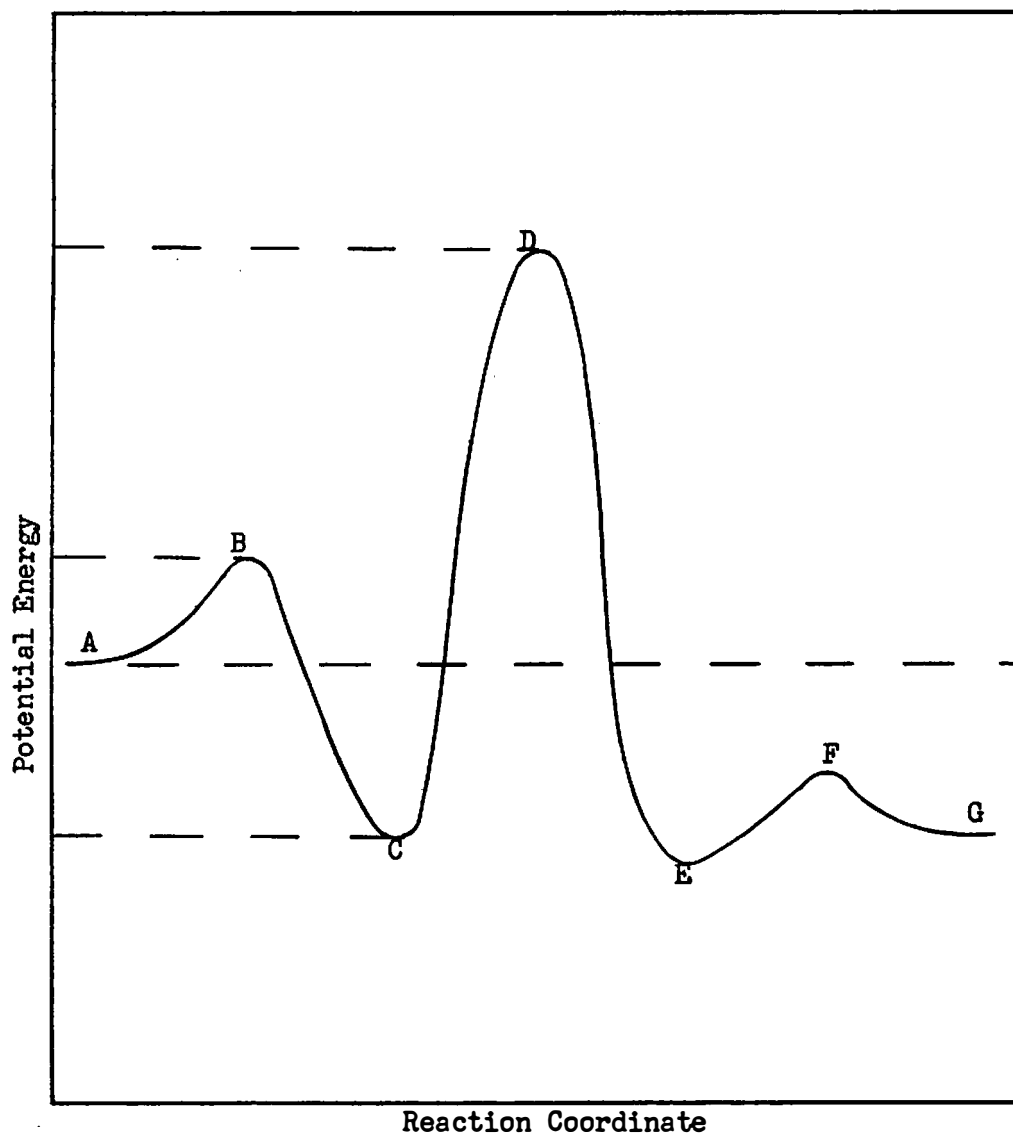


Figure 1. Plot of potential energy versus reaction coordinate .
for a reaction taking place on a catalyst surface.

It thus appears that any fundamental understanding of chemisorption and catalysis must be built upon a sound knowledge of the structure and properties of the catalyst surface. The past quarter-century has yielded a wealth of information about the properties of catalyst surfaces as well as several valuable experimental methods with which catalyst surfaces may be studied. In 1938 Brunauer, Emmett, and Teller²⁸ disclosed a reliable method with which the area of a catalyst surface may be conveniently measured. Elaborate methods have been devised for determining heats of adsorption²⁹ and entropies of adsorption.³⁰ The heat of adsorption is a direct measure of the strength of the surface-adsorbate bonds, and the entropy of adsorption is a measure of the degrees of freedom available to the adsorbed species. It should be remembered that heats and entropies of adsorption determined from calorimetric data do not necessarily represent these values for the catalytically active portions of the surface.

The transition metals have been studied extensively as catalysts in aromatic hydrogenation.³¹ These studies indicate that the activities of the metals may be attributed to two general properties: (1) surface geometry and (2) electronic properties. The effect of surface geometry has been emphasized by the multiplet theory of Balandin.^{32,33} This theory states that the catalytic activity of the various metals is due to a proper fit of one or both reactants upon the surface atoms of the catalyst. The multiplet theory readily explains why the dehydrogenation of cyclohexane to form benzene occurs only on surfaces of metals which have face-centered cubic lattices and atomic radii between 2.48 and 2.77 Å.³³

The electronic nature of the catalyst complements the surface geometry in determining catalytic activity. Beeck²⁷ has made a striking demonstration of the effect of d-band character of transition metals upon the heats of adsorption of hydrogen and ethylene and their rate of reaction with each other. In this reaction an increase in d-band character results in lower heats of adsorption and a higher reaction rate. Thus, the presence of unfilled d sublevels in the catalyst atoms appears to be a necessity for hydrogenation activity. The effect of the electronic factor and d-band character upon catalytic activity has recently been reviewed by Baker and Jenkins.³⁴

Selwood has demonstrated the effect of d-band character upon the adsorption of gases on a nickel catalyst supported on silica. Since the paramagnetism of nickel is due to the presence of unpaired 3d electrons, it would seem that if chemisorption involves the donation of electrons to the 3d sublevel, chemisorption of an electron-donor gas on the finely divided metal should result in a decrease of magnetic susceptibility. This conclusion has been verified experimentally by Selwood.³⁵ Using magnetic susceptibility measurements, he has shown that the adsorption of hydrogen and benzene on nickel results in a donation of electron density to the d band of the metal. Selwood has recently reviewed his magnetochemical work in heterogeneous catalysis.³⁶

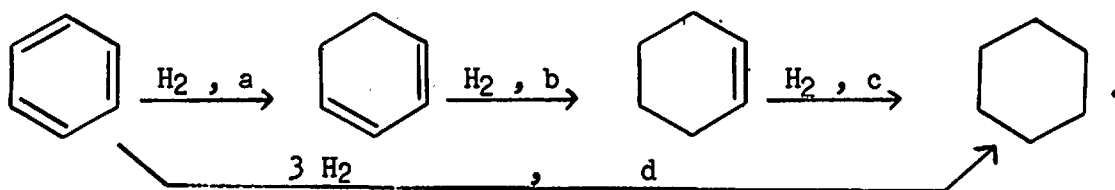
Recent investigations have shown that the work function and photoelectric emission of metal surfaces are altered quite appreciably by the adsorption of a foreign molecule. This alteration should be a measure of the change in surface electron density which results from the adsorption

of the foreign molecule. Thus, if electrons are partially donated to the surface by the adsorbate (i.e., the electron density of the surface-adsorbate bond is greater in the region of the surface) the work function will decrease and the photoelectric emission will increase. Much of the work in this area has been reviewed by Suhrmann³⁷ and by Culver and Tompkins.³⁸ For the adsorption of hydrogen on platinum, the experimental data of various researchers are in disagreement.³⁹ Some indicate a partial donation of electrons to the platinum surface by hydrogen; others indicate a partial acceptance of electrons by hydrogen. The adsorption of benzene on platinum appears to result in a partial donation of electrons to the surface.⁴⁰

It should be noticed that many of the metal-surface studies have been carried out with extremely clean surfaces; whereas, the surfaces of interest in practical catalysis are "dirty" surfaces by comparison. It is well known that small amounts of surface impurities can alter catalytic properties tremendously. This prompts one to question the validity of clean-surface studies in practical catalysis. It should not be forgotten, however, that if catalysts such as Raney nickel and Adams platinum are to be understood on a fundamental basis, the processes taking place on clean surfaces must first be understood.

D. Thermodynamics and Kinetics

Thermodynamic data reveal that the hydrogenation of the benzene nucleus is essentially irreversible at room temperature,



Accurate calorimetric data⁴¹ reveal that the heats of reaction at 355°K for the various steps are,

$$\begin{array}{ll} \text{a: } \Delta H = +5.57 \text{ kcal./mole ,} & \text{c: } \Delta H = -28.59 \text{ kcal./mole ,} \\ \text{b: } \Delta H = -26.78 \text{ kcal./mole ,} & \text{d: } \Delta H = -49.80 \text{ kcal./mole .} \end{array}$$

These data give benzene a resonance energy of 36 kcal./mole. Free energy calculations by Janz⁴² reveal that at 25° the free energy changes (ΔF) of steps a, b, c, and d are 13.2, -17.9, -18.7, -23.4 kcal./mole, respectively. Thus, at room temperature all of the steps are thermodynamically favorable except step a. As the temperature is increased, the equilibrium is steadily shifted in favor of increased unsaturation. The free energy changes (ΔF) of step d at 550 and 1000°K are 0.00 and 41.97 kcal./mole, respectively.

The chemical literature of the past thirty years contains a wealth of publications dealing either qualitatively or quantitatively with the kinetics of the hydrogenation of the benzene ring. The kinetics have been studied in both static and flow systems and with gaseous and liquid phase reduction. Unfortunately, an appreciable quantity of these studies should be regarded with considerable caution because proper attention was not paid to the effect of impurities, diffusion processes, etc. The rate of hydrogenation of benzene itself is frequently used as a criterion for evaluating the activity of a hydrogenation catalyst.

One of the first studies of the relative rates of reduction of benzene and its homologs was carried out by Adams and Marshall,⁴³ who used Adams platinum oxide as catalyst and concluded qualitatively that the rate of reduction decreased with increasing molecular weight. A similar conclusion was reached by Nikolaeva and Puckhov,⁴⁴ who reduced benzene and several of its monoalkyl derivatives over colloidal platinum at room temperature. In an investigation of the relative rates of reduction of benzene and its homologs over a nickel-alumina catalyst at temperatures of 20-200° and pressures up to 200 atmospheres, Lozovoy and Dyakova⁴⁵ found that substitution of an additional methyl group onto the ring decreases the hydrogenation rate by approximately 50 per cent. They further found that increasing the length of an alkyl group attached to the ring caused virtually no change in the rate of reduction.

Smith and Pennekamp⁴⁶ carried out a systematic study of the kinetics of the hydrogenation of benzene, monoalkylbenzenes, and polymethylbenzenes. Adams platinum oxide was used as catalyst at room temperature with 1-4 atmospheres hydrogen pressure and acetic acid being the solvent. Care was taken to insure that diffusion processes did not influence the rate of reduction. The observed kinetics were first order in hydrogen pressure and zero order in acceptor concentration. For the monoalkylbenzenes it was found that the rate decreased in the order of benzene, toluene, ethylbenzene. A depression of rate was observed for the higher alkylbenzenes only when additional carbon atoms were substituted on the carbon atom next to the ring. For the

polymethylbenzenes the rate of hydrogenation progressively decreased as the amount of nuclear substitution was increased. However, for a given degree of substitution the reduction rate increased with symmetry of substitution. Thus, the rate of hydrogenation of the xylenes decreased in the order of para, meta, ortho. This peculiar effect of symmetry of substitution upon reduction rate was also observed by Stanfield⁴⁷ in the hydrogenation of the methyl and polymethylbenzoic acids on Adams platinum oxide. The same symmetry effect has been observed in the hydrogenation of the dimethoxybenzenes⁴⁸ and the dihydroxybenzenes⁴⁹ on platinum. The effect of symmetry of substitution upon hydrogenation rate has a good experimental foundation.

As a general rule it may be stated that the rate of reduction of the benzene nucleus on metal surfaces decreases with increasing nuclear substitution. On metal sulfide catalysts, however, the opposite is true. Lozovoy and Senyavin⁵⁰ reduced several polymethylbenzenes on tungsten disulfide at 420° and 200 atmospheres pressure. These workers found that the reaction rate progressively increased as additional methyl groups were substituted onto the nucleus.

E. Stereochemistry and Mechanism

The reduction of disubstituted benzenes on metal catalysts gives stereoisomeric mixtures of which the cis isomer predominates at room temperature for the 1,2 and 1,4 disubstituted cyclohexanes, and the cis isomer predominates at all temperatures for the 1,3 disubstituted derivatives. As the reduction temperature of the 1,2 and 1,4

disubstituted benzenes is increased, the amount of trans isomer will usually increase. This is presumably due to isomerization on the catalyst surface since the trans configuration is more stable for the 1,2 and 1,4 disubstituted cyclohexanes. For the 1,3 disubstituted derivatives the cis configuration is more stable.⁵¹

Thus, there is good reason to believe that virtually all of the hydrogen approaches the benzene ring from the same side. In a series of classical investigations Linstead⁵² hydrogenated phenanthrene and diphenic acid over Adams platinum oxide in acetic acid and found that the predominant products of complete saturation (cis-syn-cis) were those which would arise from one-sided addition of hydrogen. Siegel and Dunkel⁵³ hydrogenated the xylenes over platinum in acetic acid and observed a great predominance of the cis isomer in the products although a small amount of the trans isomer was isolated. The per cent of cis isomer formed from the xylenes increased in the order of ortho, meta, para. The stereochemistry of the hydrogenation of the benzene nucleus has been reviewed by Burwell,⁵⁴ Campbell and Campbell,⁵⁵ and Kogure.⁵⁶

The mechanism by which the benzene ring is reduced on a metal surface is a highly complex and controversial subject. Various mechanisms have been proposed, and each has its own adherents and opponents. It is quite reasonable to believe that the mechanism changes from catalyst to catalyst and even on the same catalyst as the experimental conditions are varied. ✓ There is rather general agreement that the benzene ring is absorbed flatwise on the catalyst with its six pi electrons forming weak chemical bonds with the surface. Thus, the resonance of the benzene nucleus is destroyed upon adsorption.

Perhaps the two most popular mechanisms are the Langmuir-Hinshelwood^{57,58} and Rideal⁵⁹ mechanisms. The mechanism of Langmuir and Hinshelwood requires that both reactants be chemisorbed on adjacent sites of the catalyst surface. Chemisorbed hydrogen thus adds to the chemisorbed ring. The hydrogen is usually considered to add stepwise either two atoms at a time or one atom at a time. Simultaneous addition of two hydrogen atoms is referred to as the Farkas and Farkas mechanism;⁶⁰ whereas, the addition of individual hydrogen atoms is commonly called the Horiuti-Polanyi mechanism.⁶¹

The mechanism of Rideal states that it is necessary for only one of the reactants to become chemisorbed on the catalyst surface. The other reactant will then attack the chemisorbed one from the gaseous phase or van der Waals layer. Hence, if benzene is the chemisorbed reactant, the ring will be attacked by hydrogen from the side opposite the catalyst.

The multiplet theory of Balandin⁶² asserts that the nucleus, properly chemisorbed on the catalyst, is simultaneously attacked by three hydrogen molecules adsorbed on adjacent catalyst sites. This mechanism is intimately connected with the geometric arrangement of the surface atoms on the catalyst. It has been used extensively by Russian research workers.

F. Competitive Catalytic Hydrogenation

In mechanism studies of hydrogenation competitive reactions are a valuable complement to kinetic data for reduction of individual

compounds. They also provide a direct measure of the selectivity which a given catalyst possesses toward the reduction of a mixture of hydrogen acceptors. A competitive catalytic hydrogenation may be defined as one in which two or more different molecular species compete for reduction on a catalyst surface. Competitive hydrogenations may be conveniently divided into two distinct groups. In one group may be placed those hydrogenations in which one of the competing species is a reduction intermediate of another competing species. The other group will contain those reductions in which none of the competing species is a reduction intermediate of any other competing species.

The commercially-important selective reduction of acetylene to ethylene⁶³ and the reduction of cyclopentadiene to cyclopentene⁶⁴ are examples of the first category of competitive hydrogenation. The reduction of polynuclear and polyphenyl compounds are also good examples of this category. Crompton⁶⁵ studied the stepwise reduction of naphthalene, acenaphthene, and fluoranthrene on Adams platinum oxide in acetic acid. Distinct changes in kinetics were observed at specific times during the course of the reactions. On the same catalyst Alderman⁶⁶ hydrogenated diphenylmethane and diphenylacetic acid and concluded that both benzene rings were reduced at the same rate. He observed kinetics which were first order in hydrogen pressure and zero order in acceptor concentration. Shacklett^{67,68} investigated the reduction of benzilic acid and its nuclear-substituted derivatives on platinum and found that the least substituted ring was preferentially reduced. Smith, Shacklett, and Welch⁶⁹ devised a mathematical analysis of the stepwise reduction of benzilic acid. This analysis assumes an equilibrium in the competition between benzilic acid and phenylcyclohexylglycolic acid for the

catalyst surface. It permits the evaluation of the constant for this equilibrium. This constant is a quantitative measure of the relative ease of adsorption of the two acceptors on the active portion of the catalyst surface.

The reduction of binary mixtures of benzene, toluene, and polymethylbenzenes is a typical example of the second category of competitive hydrogenation. Such a series of competitive reductions has been carried out by Jungers and Wauquier,⁷⁰ who used a Raney nickel catalyst at 170° and 50 kg./cm.² pressure. Using Langmuir kinetics, they derived equations which permitted the calculation of ratios of adsorption coefficients (b_x/b_y for acceptors x and y) from infrared analyses which were carried out during the progress of the reactions. The observed kinetics were zero order in both reactants. The relative rates of reduction of the individual hydrocarbons were found to be,

benzene > toluene > para-xylene > meta-xylene > ortho-xylene ,
 whereas, the relative strengths of adsorption on the catalyst were,
 benzene > toluene > ortho-xylene > meta-xylene $\approx$ para-xylene .

In the precursor of the work recorded in this thesis,⁷¹ various binary mixtures of the xylenes were hydrogenated over platinum under essentially the same conditions as were used by Smith and Pennekamp.⁴⁶ A mathematical analysis analogous to that of Smith, Shacklett, and Welch⁶⁹ was performed upon the rate data. This analysis revealed that the relative strengths of adsorption decreased in the order of ortho, meta, para. This is the exact opposite of the relative rates of reduction of the individual xylenes.

CHAPTER II

THEORETICAL DISCUSSION

A. Competitive Hydrogenation and the Hydrogenation

Mechanism of the Benzene Nucleus

Before beginning any discussion of the mechanism by which the benzene nucleus accepts hydrogen on a metal surface, it will be expedient to define the term "reaction mechanism." A reaction mechanism embraces all of the individual collisional or other elementary processes which take place consecutively or simultaneously to produce the observed overall reaction. These processes usually involve the formation or cleavage of a chemical bond and may take place between atoms, molecules, ions, or radicals. The elucidation of a reaction mechanism should yield an intimate knowledge of the stereochemistry and relative energy content of the various intermediates and transition states which exist during the course of the reaction. Unfortunately, such an elucidation is seldom approached and never reached in the study of actual chemical reactions. A reaction mechanism is thus a theory which attempts to explain and correlate the results of experiment. As a theory it is subject to change as new experimental results are obtained.

The mechanism of the hydrogenation of the benzene nucleus thus involves a detailed description of the intermediates which exist on the catalyst surface during the course of the reaction. It also involves the sequence in which these intermediates are formed and

in which they interact with each other and the surface atoms of the catalyst. In its most sophisticated form the mechanism would provide a complete picture of what a hypothetical Maxwellian demon would "see" if he were present on the catalyst surface during the course of the reaction.

Since the mechanism of a reaction on a catalyst surface may be extremely sensitive to variations in catalyst composition and reaction conditions, it should be remembered that the results of experiments carried out under a given set of reaction parameters (catalyst, temperature, etc.) are not necessarily valid when one or more of the parameters are changed. In many instances it is profitable to speak of the common characteristics which the reduction of the benzene nucleus has on various metal catalysts under different experimental conditions and to assume that experiments carried out with one catalyst may be used in interpreting the mechanism on another catalyst. This practice, however, should be followed only with a full realization of the hazards involved in its use.

A convenient starting point for the elucidation of the hydrogenation mechanism of benzene and its derivatives is the valid kinetic data of Smith and Pennekamp.⁴⁶ These investigators have found that on platinum in glacial acetic acid at room temperature and hydrogen pressures of one to four atmospheres the kinetics are clearly first order in hydrogen pressure and zero order in acceptor concentration. Since these kinetics are determined by the slow (rate-determining) step of the reaction sequence, it will be profitable to examine the various steps which may compose this sequence:

- (1) Absorption of hydrogen from the gaseous phase into the liquid phase;
- (2) Diffusion of hydrogen through the solution to the catalyst surface;
- (3) Diffusion of acceptor through the solution to the catalyst surface;
- (4) Adsorption of hydrogen on catalyst surface;
- (5) Adsorption of acceptor on catalyst surface;
- (6) Reaction of hydrogen and acceptor on catalyst surface;
- (7) Desorption of product;
- (8) Diffusion of product away from catalyst surface.

If a Rideal mechanism is operating, either step four or step five will not take place since it will be necessary for only one reactant to be chemisorbed prior to undergoing reaction. In addition, step six will be replaced by a step embracing the attack of one chemisorbed reactant by the other reactant from the van der Waals layer.

An examination of the above eight steps reveals that it will only be possible for certain of them to be the rate-determining one. Steps one, two, and three may be ruled out as affecting the overall reduction rate since the experimental conditions are such that diffusion processes do not affect the reaction rate. This is apparent since the rate of hydrogenation is directly proportional to the catalyst weight and independent of the rate of agitation of the reaction mixture. Similarly, step eight may be excluded from being rate-determining. Since the masses and the volumes occupied by the benzene ring and the cyclohexane ring are of comparable magnitude, it seems logical to

conclude that if migration of the benzene nucleus to the catalyst surface does not affect the reaction rate, migration of the cyclohexane ring away from the surface will have no effect upon the rate.

The reaction kinetics show that step five, adsorption of acceptor, is not rate-determining. If step five were rate-determining, the observed kinetics would be first order in acceptor concentration and zero order in hydrogen pressure. Since these kinetics are contrary to experiment, the adsorption of the benzene nucleus on the catalyst must be a fast step. Thus, there is an equilibrium between acceptor in solution and acceptor adsorbed on the catalyst surface.

If step seven, desorption of product, were rate-determining, product inhibition would be observed. Cross⁷² hydrogenated benzene over platinum in glacial acetic acid in the presence of varying amounts of cyclohexane. The presence of cyclohexane had no effect upon the reduction rate of benzene. In a similar manner it has been shown⁷³ that cyclohexanecarboxylic acid does not reduce the hydrogenation rate of benzoic acid. This lack of product inhibition thus leads to the conclusion that product desorption is a fast step. Corroborating evidence for this conclusion is provided by the reaction kinetics. If product desorption were the slow step, the experimental kinetics would most likely be first order in acceptor concentration rather than zero order.

Examination of the kinetic data reveals that step four, adsorption of hydrogen, may be the slow step. The operation of a Langmuir-Hinshelwood mechanism would thus require that adsorption of hydrogen on the active spots of the catalyst be rate-determining. The operation of a Rideal mechanism necessitates that the slow step be either the

attack of strongly chemisorbed benzene by hydrogen from the van der Waals layer or the adsorption of hydrogen on the active spots of the surface followed by rapid attack of benzene from the van der Waals layer.

Assuming hydrogen chemisorption to be rate-determining, the following expression is valid:

$$\text{rate} = k_r C_H, \quad (1)$$

where k_r and C_H are the intrinsic rate constant and hydrogen concentration in solution, respectively. The hydrogen concentration and hydrogen pressure (P) are related by Henry's law since there is an equilibrium between hydrogen in the two phases,

$$C_H = k_H P, \quad (2)$$

where k_H is the Henry's law constant for a given reaction temperature. Thus the experimental rate is related to the hydrogen pressure by,

$$\text{rate} = k_r k_H P = k_e P, \quad (3)$$

and the experimental rate constant (k_e) is equal to the product $k_r k_H$.

At first glance the assumption of the rate-determining step being the adsorption of the hydrogen appears to imply that the rates of hydrogenation of the individual hydrocarbons should be the same. The variation of the rate of reduction of the individual hydrocarbons does not contradict the existence of hydrogen adsorption as the rate-determining step. If flatwise adsorption of the benzene ring is assumed, and there is good evidence that this is the case,³⁵ the amount of surface area covered by the chemisorption of the benzene nucleus will increase as substitution on the nucleus is increased. This increase in nuclear substitution will effectively decrease the active surface area available for hydrogen chemisorption and result in a lower rate

of hydrogen chemisorption and a lower experimental rate. At the same time the kinetics for the reduction of the individual acceptors may still be first order in hydrogen and zero order in acceptor. It is also logical to believe that the degree and symmetry of nuclear substitution will affect the "packing" of the acceptor molecules on the active portion of the catalyst. Thus, as the degree of nuclear substitution is increased, fewer acceptor molecules will be adsorbed on the same physical area of the active catalyst.

Assuming step six, the reaction between hydrogen and the benzene nucleus on the catalyst surface, to be rate-determining will also yield accord with the kinetic data. In this case a Langmuir-Hinshelwood mechanism must be operating since both reactants are chemisorbed on the catalyst surface. Further, the addition of the first molecule of hydrogen will embrace the slow step. If the addition of the second molecule were rate-determining, second-order kinetics in hydrogen would be observed. Similarly, third-order kinetics in hydrogen would be observed if the slow step involved either the addition of the third molecule of hydrogen or the simultaneous addition of three molecules of hydrogen as is postulated by the multiplet theory.

Step six can best be rationalized as the slow step by resorting to classical Langmuir kinetics. According to Langmuir kinetics,⁷⁴ there will be equilibria between gaseous hydrogen and hydrogen chemisorbed on the catalyst surface and between acceptor in solution and acceptor chemisorbed on the catalyst surface. The rate of reaction will be proportional to the fraction of catalyst surface covered by each reactant,

$$\text{rate} = k_1 \theta_H \theta_a, \quad (4)$$

where k_1 , θ_H , and θ_a are the intrinsic rate constant, fraction of surface covered by hydrogen, and fraction of surface covered by acceptor, respectively. If it is assumed that hydrogen and benzene do not compete with each other for the same catalyst sites, the following expressions result for θ_H and θ_a :

$$\theta_H = \frac{b_H P}{1 + b_H P}, \quad (5)$$

$$\theta_a = \frac{b_a C_a}{1 + b_a C_a}, \quad (6)$$

where b_H , b_a , and C_a are adsorption coefficient of hydrogen, adsorption coefficient of acceptor, and acceptor concentration, respectively. Thus, the rate expression will be,

$$\text{rate} = k_1 \left[\frac{b_H P}{1 + b_H P} \right] \left[\frac{b_a C_a}{1 + b_a C_a} \right]. \quad (7)$$

If the acceptor is very strongly adsorbed on its portion of the active surface, θ_a will approach unity, and unity will be negligible in comparison to $b_a C_a$. If hydrogen is very weakly adsorbed upon its portion of the active surface, θ_H will approach zero, and $b_H P$ will be negligible in comparison to unity. The rate equation will thus reduce to,

$$\text{rate} = k_1 b_H P. \quad (8)$$

Equation (8) is in the same form as the experimental rate equation where the experimental rate constant is the product, $k_1 b_H$.

Thus, the kinetics of the hydrogenation of the individual benzenes reveal that the rate-determining step may be the adsorption of hydrogen on the active spots of the surface, the surface interaction

of the strongly adsorbed nucleus with weakly adsorbed hydrogen, or the attack of the chemisorbed nucleus by hydrogen from the van der Waals layer. It is now in order to devise further experiments which will aid in deciding which of these steps is the slow one and in distinguishing between a Langmuir-Hinshelwood and Rideal mechanism. Competitive reduction of various binary mixtures of acceptors under the same conditions as were used for the individual acceptors should be such an experiment.

An even more valuable result of binary competitive hydrogenation should be a deeper insight into the mystery surrounding the relationship between the structure of the acceptor and its hydrogenation rate. As was stated in chapter I, the rate of reduction decreases with increasing nuclear substitution and increases with symmetry of substitution for a given degree of nuclear substitution. It has been suggested⁴⁶ that these effects may be related to the "fit" of the acceptor on the catalyst surface or to the steric hindrance which the substituents offer toward hydrogen approaching the nucleus. The fundamental question involved is, "Are the relative rates of reduction of substituted benzenes a result of their relative strengths of adsorption on the catalytically active portion of the surface or of their relative reactivity per se on this surface?"

B. Mathematical Analysis

The proper evaluation and assimilation of the competitive hydrogenation data of binary mixtures of benzene and its derivatives

in acetic acid solution in a closed system requires a suitable mathematical analysis. This analysis should be based on postulates which indicate certain mechanistic properties of the reaction. It should yield equations which can be conveniently tested with the experimental data. Further, these tests should be in mutual agreement. The possibility of two or more explanations for the experimental data should always be kept in mind.

The first postulate of this analysis is that both acceptors obey the Langmuir adsorption isotherm and compete for the same catalyst surface. This postulate is made with full cognizance of the heterogeneity which many catalyst surfaces have.⁷⁵ The use of the Langmuir isotherm assumes a uniform surface with localized adsorption and no interaction between the adsorbed molecules. Although adsorption studies have shown that the surface of metallic platinum is heterogeneous, Kwan⁷⁶ has produced good evidence that the catalytically active portion of a platinum surface is essentially homogeneous. Thus, under a given set of experimental conditions the activity of the catalytically active portion of a platinum surface may be uniform. Balandin²⁶ in his theory of quasi-homogeneous surfaces has shown that in competitive reactions the surface may be heterogeneous as long as the ratio of the adsorption coefficients of the strongly adsorbed competing reactants remains a constant value on the various regions of the active surface.

For the competitive hydrogenation of acceptors A and B, the Langmuir adsorption isotherm⁷⁷ yields for the fraction of surface covered by A (σ_A),

$$\sigma_A = \frac{b_A C_A}{1 + b_A C_A + b_B C_B} \quad , \quad (9)$$

and for the fraction covered by B (σ_B),

$$\sigma_B = \frac{b_B C_B}{1 + b_A C_A + b_B C_B} \quad , \quad (10)$$

where b and C represent adsorption coefficients and acceptor concentrations, respectively. The second postulate is that both acceptors are strongly adsorbed on the catalytically active portion of the surface.

Thus,

$$(b_A C_A + b_B C_B) \gg 1 \quad . \quad (11)$$

Equations (9) and (10) may now be modified to yield,

$$\sigma_A = \frac{b_A C_A}{b_A C_A + b_B C_B} \quad , \quad (12)$$

$$\sigma_B = \frac{b_B C_B}{b_A C_A + b_B C_B} \quad . \quad (13)$$

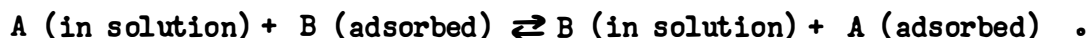
Dividing equation (12) by equation (13) gives,

$$\frac{\sigma_A}{\sigma_B} = \frac{b_A C_A}{b_B C_B} \quad , \quad (14)$$

which may be rearranged to,

$$\frac{b_A}{b_B} = \frac{\sigma_A C_B}{\sigma_B C_A} = K_{AB} \quad . \quad (15)$$

Since b_A and b_B are both equilibrium constants, each being a ratio of rate constants, K_{AB} is a true equilibrium constant and is thus a function of temperature only. K_{AB} is the equilibrium constant for the reaction,



In its capacity as an equilibrium constant K_{AB} may be used to calculate the standard free energy change (ΔF^0) for the above reaction; the temperature gradient of K_{AB} may be used to calculate the standard enthalpy change (ΔH^0) of the reaction.

Another useful equation is obtained by adding equations (12) and (13),

$$\sigma_A + \sigma_B = 1 . \quad (16)$$

This equation simply states that all of the active surface upon which acceptor molecules may be chemisorbed is covered by either molecules of A or B. Equations (15) and (16) may also result from an alternate set of postulates which state,⁷¹

- (1) The two acceptors compete for the same catalyst surface upon which each would react if the other were completely absent;
- (2) Adsorption of products and solvent on the catalytically active portion of the surface is negligible in the presence of acceptors;
- (3) A rapid and reversible equilibrium exists between acceptors on the catalyst surface and acceptors in solution.

The derivation of equations (15 and (16) from the Langmuir adsorption isotherm gives them a more solid theoretical foundation.

The third postulate is that the reaction mechanism is the same for a competitive hydrogenation of acceptors A and B as it is for the reduction of each individual acceptor. The reductions of A and B are

fundamentally the same reaction since in each case a benzene ring is being reduced to a cyclohexane ring. It is thus logical to conclude that the same form of rate equation is valid for the reduction of pure A, pure B, and binary mixtures of A and B. For the reduction of a pure acceptor, A for example, in glacial acetic acid solution in a closed reaction system of volume V_s under conditions of equilibrium shaking, the following rate equation is valid for the variation of hydrogen pressure (P) with time (t):

$$\frac{dP}{dt} = \frac{-W_c k_A}{V_s S} P, \quad (17)$$

where W_c and S are catalyst weight and catalyst standardization factor, respectively. k_A is the standard first-order rate constant for acceptor A. A similar rate equation is valid for the reduction of pure B; it contains an expression for k_B , the standard first-order rate constant of B.

For the reduction of a binary mixture of A and B the following rate equation is valid:

$$\frac{dP}{dt} = - \frac{W_c}{V_s S} (k_A \sigma_A + k_B \sigma_B) P. \quad (18)$$

$k_A \sigma_A$ is the contribution to the total rate by the reduction of A, and $k_B \sigma_B$ is the contribution by the reduction of B. Thus, the rate of disappearance of a given acceptor depends upon its intrinsic rate of reduction (standard rate constant) and the fraction of the active catalyst surface it occupies. Since σ_A and σ_B are variables, the quantity $(k_A \sigma_A + k_B \sigma_B)$ is not necessarily a constant.

The stoichiometry of the reduction of the benzene nucleus, three molecules of hydrogen per nucleus, may be profitably applied to

competitive hydrogenation. This application may be considered as the fourth postulate. Thus, for the competitive reduction of acceptors A and B,

$$3 \, dn_A = \alpha_A dn_H \quad , \quad (19)$$

where n_A and n_H are the number of moles of A and hydrogen, respectively, in the reaction system. α_A is the fraction of hydrogen undergoing reaction between times t and $t + dt$ which is taken up by acceptor A. Since A and B are both reduced according to the same kinetics, α_A may be defined thusly,

$$\alpha_A = \frac{k_A \sigma_A}{k_A \sigma_A + k_B \sigma_B} \quad . \quad (20)$$

Similarly, α_B may be defined,

$$\alpha_B = \frac{k_B \sigma_B}{k_A \sigma_A + k_B \sigma_B} \quad . \quad (21)$$

Hence, it is obvious that,

$$\alpha_A + \alpha_B = 1 \quad . \quad (22)$$

Equation (19) may thus be written,

$$3 \, dn_A = \left(\frac{k_A \sigma_A}{k_A \sigma_A + k_B \sigma_B} \right) dn_H \quad . \quad (23)$$

The fifth and final postulate assumes the ideal behavior of gaseous hydrogen under the experimental conditions (room temperature and two to four atmospheres pressure). Thus, at absolute temperature T ,

$$PV_S = n_H RT \quad , \quad (24)$$

where R is the universal gas constant. Since T and V_S are constant,

$$dn_H = \frac{V_S}{RT} dP \quad . \quad (25)$$

The molar concentration of A in volume of solution V_1 is related to n_A by,

$$C_A = \frac{n_A}{V_1} \quad ; \quad (26)$$

simple differentiation reveals that,

$$dn_A = V_1 dC_A \quad . \quad (27)$$

Substituting equations (25 and (27) into equation (23),

$$dC_A = \frac{V_s}{3V_1 RT} \left(\frac{k_A \sigma_A}{k_A \sigma_A + k_B \sigma_B} \right) dP \quad . \quad (28)$$

Using exactly the same scheme of reasoning for acceptor B yields,

$$dC_B = \frac{V_s}{3V_1 RT} \left(\frac{k_B \sigma_B}{k_A \sigma_A + k_B \sigma_B} \right) dP \quad . \quad (29)$$

Equations (15), (16), (18), (28), and (29) constitute a set of five independent equations none of which can be derived from the other four. These equations may be used in the analysis of binary competitive hydrogenation data of benzene and its derivatives. For a given competitive hydrogenation these five equations contain six parameters. The mathematical treatment embodied in these equations is fundamentally the same as that used by Jungers and Wauquier.⁷⁰ If both sides of equations (28) and (29) are divided by dt and the resulting equations are substituted into equation (18), the following two equations are obtained:

$$\frac{dC_A}{dt} = - \left(\frac{W_c}{3V_1 RTs} \right) k_A \sigma_A^P \quad , \quad (30)$$

$$\frac{dC_B}{dt} = - \left(\frac{W_c}{3V_1 RTs} \right) k_B \sigma_B^P \quad . \quad (31)$$

These equations are fundamentally the same as the one used by Jungers and Wauquier. In addition, they clearly depict the presence of Langmuir

kinetics and the dependence of the rate of disappearance of each reactant upon its intrinsic rate and its fraction of surface coverage.

In the forerunner of the work reported in this thesis,⁷⁸ the following equation has been derived for the competitive hydrogenation of benzeneoid acceptors A and B:

$$\frac{d(k_A \sigma_A + k_B \sigma_B)}{dt} = \left[\frac{W_c}{JRTSV_1} \right] \left[\frac{P \sigma_B \sigma_A}{C_B + K_{AB} C_A} \right] (k_B - k_A) (K_{AB} k_A - k_B) \quad (32)$$

This equation gives the theoretical rate of change of the slope of a first order kinetics plot ($\log P$ versus time) for the reduction of a given binary mixture of A and B.

The main purpose, however, of the mathematical analysis of the competitive hydrogenation data is the quantitative evaluation of K_{AB} , the competitive adsorption equilibrium constant. K_{AB} is of extreme interest because it provides a direct measure of the relative ease of adsorption of the acceptors on the active spots of the catalyst. Since the parameters P , t , C_A , and C_B appear to be susceptible to direct measurement during the course of a given competitive hydrogenation, it is quite reasonable to expect that K_{AB} can be evaluated from a knowledge of these parameters during the course of the hydrogenation.

If equation (16) is substituted into equation (18),

$$\frac{dP}{dt} = - \frac{W_c}{V_S S} (k_A + k_B \sigma_B - k_A \sigma_B) P \quad , \quad (33)$$

which upon rearrangement yields,

$$\sigma_B = \frac{- \left(\frac{V_S S}{W_c P} \right) \frac{dP}{dt} - k_A}{k_B - k_A} \quad . \quad (34)$$

Substituting equation (16) into equation (15),

$$K_{AB} = \frac{(1 - \sigma_B)C_B}{\sigma_B C_A} \quad , \quad (35)$$

which rearranges to,

$$\sigma_B = \frac{C_B}{K_{AB}C_A + C_B} \quad . \quad (36)$$

Equating equations (34) and (36),

$$\frac{C_B}{K_{AB}C_A + C_B} = \frac{-\left(\frac{V_g S}{W_c P}\right)\left(\frac{dP}{dt}\right) - k_A}{k_B - k_A} \quad . \quad (37)$$

This equation rearranges to,

$$K_{AB} = \frac{C_B}{C_A} \frac{\left[k_B + \left(\frac{V_g S}{W_c P}\right)\frac{dP}{dt}\right]}{\left[k_A - \left(\frac{V_g S}{W_c P}\right)\frac{dP}{dt}\right]} \quad . \quad (38)$$

K_{AB} may thus be approximately evaluated by taking a small finite reaction increment and assuming that the average rate of pressure drop during this increment, $\Delta P/\Delta t$, is equal to dp/dt . P , C_B , and C_A should be measured at the mid-point of this reaction increment. In practice, the use of equation (38) yields results with large experimental error. This error results primarily from the differences which are taken between two numbers of comparable magnitude in both numerator and denominator. Thus, the error in each of the two numbers (up to 5 per cent) is greatly magnified in the final value of K_{AB} .

A more satisfactory method of evaluating K_{AB} results from dividing equation (28) by equation (29) to yield,

$$\frac{dC_A}{dC_B} = \frac{k_A \sigma_A}{k_B \sigma_B} \quad . \quad (39)$$

Substituting equation (15) into equation (39),

$$\frac{dC_A}{dC_B} = \left(\frac{K_{AB}k_A}{k_B} \right) \frac{C_A}{C_B} \quad . \quad (40)$$

Equation (40) may be integrated thusly,

$$\int_{C_A^0}^{C_A} \frac{dC_A}{C_A} = \frac{K_{AB}k_A}{k_B} \int_{C_B^0}^{C_B} \frac{dC_B}{C_B} \quad , \quad (41)$$

where C_A^0 and C_B^0 are the initial concentrations of A and B, respectively.

Performing the integration,

$$\ln \frac{C_A}{C_A^0} = \frac{K_{AB}k_A}{k_B} \ln \frac{C_B}{C_B^0} \quad . \quad (42)$$

Changing to common logarithms and rearranging yields,

$$\log C_A = \frac{k_A K_{AB}}{k_B} \log C_B + \left(\log C_A^0 - \frac{k_A K_{AB}}{k_B} \log C_B^0 \right) \quad . \quad (43)$$

An inspection of equation (43) reveals that the quantity within parentheses on the right side of the equation is a constant for a given competitive hydrogenation. Thus, a plot of $\log C_A$ versus $\log C_B$ should yield a straight line of slope $k_A K_{AB}/k_B$. Such a plot should be a test of the validity of the mathematical analysis which leads to equation (43). Since k_A and k_B can be determined from the hydrogenation of the individual acceptors, K_{AB} may be evaluated from the slope of the straight line. Actually, it is only necessary to know the ratio of k_A and k_B in order to evaluate K_{AB} from the plot. It should be remembered that equation (43) is a general equation for competitive hydrogenation as long as the stoichiometry and the form of rate equations are the same for both A and B. Equation (43) may also be applied to a series of competitive hydrogenations of a given mixture of A and B which are carried out to different degrees of reaction.

Thus, it is seen that equations (38) and (43) give two independent methods of determining the competitive adsorption equilibrium constant, K_{AB} . These two methods should give agreement within experimental error. A further check of the K_{AB} values may be obtained by competitively hydrogenating A and then B against a third acceptor, C. For the competitive hydrogenation of A and C,

$$K_{AC} = \frac{\sigma_A^C C_C}{\sigma_C^C C_A} = \frac{b_A}{b_C} \quad , \quad (44)$$

and for the competitive hydrogenation of B and C,

$$K_{BC} = \frac{\sigma_B^C C_C}{\sigma_C^C C_B} = \frac{b_B}{b_C} \quad . \quad (45)$$

Therefore,

$$\frac{K_{AC}}{K_{BC}} = \frac{b_A/b_C}{b_B/b_C} = \frac{\sigma_A^C C_C / \sigma_C^C C_A}{\sigma_B^C C_C / \sigma_C^C C_B} \quad , \quad (46)$$

$$\frac{K_{AC}}{K_{BC}} = \frac{b_A}{b_B} = \frac{\sigma_A^C C_B}{\sigma_B^C C_A} = K_{AB} \quad . \quad (47)$$

Whether K_{AC} and K_{BC} are multiplied or divided to obtain K_{AB} will depend upon how they are defined. Several independent evaluations of K_{AB} can arise from series of competitive hydrogenations of this type.

CHAPTER III

EXPERIMENTAL

A. Materials

1. Platinum Oxide Catalyst

The platinum oxide catalyst used in all hydrogenation runs was obtained from the Baker Catalyst Company of Newark, New Jersey. It was sifted through a 325-mesh sieve and then mechanically agitated for several days to insure adequate mixing. To correct for possible differences in catalyst activity, each sample of catalyst was standardized by hydrogenation with benzoic acid. A standardization factor (S) was evaluated for each catalyst sample. This was the factor by which the experimental first-order rate constant for benzoic acid was multiplied in order to give a value of $0.1120 \text{ min.}^{-1} \text{g.}^{-1}$. All rate constants obtained thereafter with the same catalyst sample were corrected by the factor S so that standard rate constants were obtained. The activity of all of the catalyst samples used in this work was the same within experimental error.

2. Acetic Acid

Du Pont reagent grade glacial acetic acid was used as solvent in all hydrogenation runs. It was fractionally distilled through an 8-ft. Vigreux column, with the fraction used distilling at 117.6° at

742 mm. mercury pressure.* Undistilled reagent grade glacial acetic acid was used as solvent in all spectrophotometric analyses. Absorbancy readings in the ultraviolet region of the spectrum showed no difference between the distilled and undistilled acid.

3. Hydrogen

Hydrogen was obtained from Welding Gas Products Company of Chattanooga, Tennessee. It was used directly from the cylinder. Previous experiments had shown that further purification was unnecessary.⁷⁹

4. Benzoic Acid

Eastman white-label grade benzoic acid was used to standardize all catalyst samples. It was used without further purification. Its melting point was 122.7-123.0°.

5. Benzene

Fisher certified reagent grade benzene was fractionally distilled in a 12-ft. column packed with glass helices at a reflux ratio of 30:1. A middle fraction was used for hydrogenation studies. It was collected at a constant head temperature of 79.6° at 750 mm. mercury pressure. Its refractive index, n_D^{25} , was 1.4981. These physical constants check favorably with the American Petroleum Institute tables,⁸⁰ which give an n_D^{25} value of 1.49792 and a boiling point which may be corrected to 79.7° at 750 mm. mercury pressure.

*All boiling-point and melting-point values given in this work were taken with calibrated Anschütz thermometers. They are corrected for stem exposure unless otherwise noted. All pressure readings are corrected to 0° for the brass scale.

6. Toluene

Fisher certified reagent grade toluene was fractionally distilled through the same column which was used for the purification of benzene. A middle fraction was collected at a reflux ratio of 30:1 and a constant head temperature of 109.7° at 742 mm. mercury pressure. Refractive index, n_D^{25} , of sample was 1.4941. The American Petroleum Institute tables⁸⁰ give for toluene a refractive index, n_D^{25} , of 1.49413 and a boiling point which may be corrected to 109.8° at 742 mm. mercury pressure.

7. ortho-Xylene

The ortho-xylene used in this research was obtained from the previous work by Shacklett.⁶⁸ It was Cronite commercial grade ortho-xylene and had been purified by fractional distillation, azeotropic distillation with 2-methoxyethanol,⁸¹ and subsequent redistillation. Thus, the sample as obtained was quite pure. It was distilled through the same column as was used in the purification of benzene and toluene at a reflux ratio of 20:1. The fraction used in the hydrogenation studies distilled at 143.6° at 744 mm. mercury pressure and had a refractive index, n_D^{25} , of 1.5029. The American Petroleum Institute tables⁸⁰ give for ortho-xylene an n_D^{25} value of 1.50295 and a boiling point which may be corrected to 143.6° at 744 mm. mercury pressure.

8. meta-Xylene

Appreciable difficulty was encountered in the attempts to purify meta-xylene. A sample of Eastman white-label grade meta-xylene which had previously been distilled by Shacklett⁶⁸ was redistilled. The

sample did not give a constant head temperature and gave low refractive index readings. It was finally discovered that meta-xylene could be purified by selective sulfonation. This method deals with the reaction of an excess of impure meta-xylene with concentrated sulfuric acid and is based upon the fact that meta-xylene is more susceptible toward electrophilic substitution than its contaminants. The meta-xylene sulfonic acid thus formed is then hydrolyzed back to pure meta-xylene. This principle has previously been used by Orlov⁸² and by Patterson, McMillan and Somerville.⁸³ The experimental procedure is given in the precursor of this work.⁸⁴ The product from this purification procedure was distilled through a 10-ft. Vigreux column at a reflux ratio of 80:1. It had a boiling point of 138.4° at 743 mm. of mercury and a refractive index, n_D^{25} , of 1.4946. The American Petroleum Institute tables⁸⁰ give for meta-xylene a refractive index, n_D^{25} , of 1.49464 and a boiling point of 138.3° when corrected to 743 mm. mercury pressure.

9. para-Xylene

The sample of para-xylene used in the hydrogenation studies was the Eastman white-label grade chemical which had previously been distilled by Shacklett.⁶⁸ The best sample from this distillation was again fractionated through a 10-ft. Vigreux column at a reflux ratio of 60:1. The sample was collected at a constant head temperature of 137.4° at 741 mm. mercury pressure. It had a refractive index, n_D^{25} , of 1.4933. The American Petroleum Institute tables⁸⁰ give an n_D^{25} value of 1.49325 and a boiling point which may be corrected to 137.4° at 741 mm. mercury pressure.

10. Hemimellitene (1,2,3-Trimethylbenzene)

A hemimellitene sample was obtained from the synthetic work of Shacklett.⁶⁸ It had been prepared by chloromethylation of ortho-xylene and subsequent hydrogenolysis with lithium aluminum hydride. The hemimellitene sample had previously been sulfonated, recrystallized three times as the sulfonic acid, hydrolyzed back to the hydrocarbon, steam distilled, and fractionally distilled. Thus, it is understandable why a simple distillation through a 10-ft. Vigreux column at a reflux ratio of 75:1 yielded a pure sample of hemimellitene. The boiling point of the resulting product was 175.1° at 741 mm. mercury pressure. Its refractive index, n_D^{25} , was 1.5115. According to the tables of the American Petroleum Institute,⁸⁰ n_D^{25} is 1.51150, and the boiling point at 741 mm. mercury pressure is 175.1°.

11. Pseudocumene (1,2,4-Trimethylbenzene)

The pseudocumene used in this work was prepared by Shacklett.⁶⁸ It was prepared by chloromethylation of meta-xylene and para-xylene and subsequent hydrogenolysis by lithium aluminum hydride. The pseudocumene sample had previously been purified by a procedure of sulfonation, recrystallization, and hydrolysis similar to that used in the purification of hemimellitene. It was distilled through a 12-ft. glass-helix-packed column at a reflux ratio of 80:1. The product had a boiling point of 168.6° at 744 mm. mercury pressure and a refractive index, n_D^{25} , of 1.5024. The American Petroleum Institute tables⁸⁰ give pseudocumene a refractive index, n_D^{25} , of 1.50237 and a boiling point which may be corrected to 168.5° at 744 mm. mercury pressure.

12. Mesitylene (1,3,5-Trimethylbenzene)

The mesitylene sample used in the hydrogenation studies was also a Shacklett preparation.⁶⁸ It was prepared by the acid-catalyzed self condensation of acetone. The mesitylene sample had previously been purified by sulfonation, recrystallization, steam distillation, and fractional distillation. All that was necessary to obtain a pure sample was a simple distillation through a 10-ft. Vigreux column at a reflux ratio of 50:1. The mesitylene distillate had a refractive index, n_D^{25} , of 1.4969 and a boiling point of 164.0° at 746 mm. mercury pressure. These physical constants are in agreement with the tables of the American Petroleum Institute⁸⁰ which give n_D^{25} as 1.49684 and the boiling point at 746 mm. mercury pressure as 164.0°.

13. Prehnitene (1,2,3,4-Tetramethylbenzene)

Prehnitene was redistilled through a 10-ft. Vigreux column at a reflux ratio of 80:1. It had previously been synthesized by Shacklett⁶⁸ via bischloromethylation of ortho-xylene and subsequent hydrogenolysis with lithium aluminum hydride. The prehnitene sample distilled at a constant head temperature of 204.0° at 743 mm. mercury pressure. Its refractive index, n_D^{25} , was 1.5181. The American Petroleum Institute tables⁸⁵ give an n_D^{25} value of 1.5181 and a boiling point which may be corrected to 204.1° at 743 mm. mercury pressure.

14. Isodurene (1,2,3,5-Tetramethylbenzene)

Isodurene was obtained from the synthetic work of Shacklett,⁶⁸ who chloromethylated mesitylene, hydrogenolyzed the product with

lithium aluminum hydride, and isolated isodurene by means of fractional distillation. The isodurene sample was distilled through a 10-ft. Vigreux column at a reflux ratio of 80:1. The boiling point of the distillate was 197.5° at 750 mm. mercury pressure, and its refractive index, n_D^{25} , was 1.5110. According to the American Petroleum Institute tables,⁸⁵ n_D^{25} is 1.5107, and the boiling point at 750 mm. mercury pressure is 197.5° .

15. Durene (1,2,4,5-Tetramethylbenzene)

The durene sample used in the hydrogenation studies was also a preparation of Shacklett.⁶⁸ It was prepared by bischloromethylation of para-xylene and chloromethylation of pseudocumene. The product had been isolated by subsequent hydrogenolysis and recrystallization. Pure durene was obtained by recrystallizing Shacklett's preparation from 95 per cent ethanol according to the procedure of Smith.⁸⁶ Its melting point was $79.4-79.9^{\circ}$. The American Petroleum Institute tables⁸⁵ give a melting point of 79.2° .

16. Pentamethylbenzene

The purification of pentamethylbenzene presented appreciable difficulty. Both sublimation and distillation were used without success. A reasonably pure product was obtained by a series of recrystallizations. Eastman white-label grade pentamethylbenzene (melting point, $50.8-53.0^{\circ}$) was successively recrystallized from redistilled absolute alcohol, reagent grade toluene, and redistilled reagent grade methanol. The melting point of the product progressively

rose after each recrystallization. After drying overnight in a desiccator, the pentamethylbenzene sample melted at 53.5-55.1°. The American Petroleum Institute tables⁸⁷ give a melting point of 54.3°. Vapor-phase chromatographic analysis showed the sample to be free of hexamethylbenzene and tetramethylbenzenes, which are the principal contaminants of pentamethylbenzene.⁸⁶

17. Hexamethylbenzene

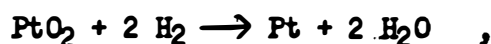
Hexamethylbenzene was prepared according to the method of Cullinane, Chard, and Dawkins.⁸⁸ The preparation and purification were carried out according to the procedure which follows.

A glass column, 30 in. high and 19 mm. in diameter, was loaded with 8-14 mesh alumina. The alumina was activated by passing nitrogen through the column at 400°. Fifty grams of phenol was dissolved in 500 ml. of methanol. Using a dropping funnel, the solution was admitted to the column at a rate of approximately 2 ml. per minute as the column was maintained at a temperature 410°C. A yellow product consisting of crude hexamethylbenzene, 60.7 g., was obtained from the bottom of the column. This product was decolorized with Norit decolorizing carbon and recrystallized from a mixture of 600 ml. of ethanol (95 per cent) and 200 ml. of benzene. The resulting crystals, 40.6 g., melted at 157-160° (uncorrected). A second recrystallization was carried out from 600 ml. of ethanol-benzene solution of the same composition as above. The hexamethylbenzene solution was decolorized twice before precipitation to yield 17.8 g. of product which melted at 164-165°

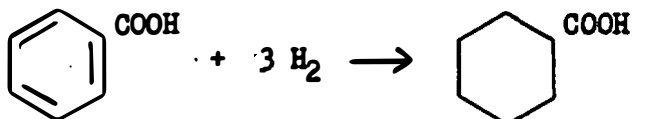
(uncorrected). A final recrystallization was carried out from reagent grade benzene. After drying in a vacuum desiccator, the pure hexamethylbenzene sample gave a melting point of 166.1-166.8°. Gas-phase chromatographic analysis showed it to be free of contaminants.

B. Hydrogenation Apparatus

A Paar low-pressure hydrogenation apparatus with certain modifications was used for all hydrogenation runs. The hydrogen reserve tank was replaced by a straight connection. This reduced the volume of the reaction system and gave a larger pressure drop for the reduction of a given quantity of acceptor. The volume of the reaction system was determined by hydrogenating a known quantity of benzoic acid in the presence of a known quantity of platinum oxide catalyst. The ideal gas law was then applied to the stoichiometric relations involved. The equation for the reduction of the catalyst was,



and that for the reduction of benzoic acid was,



It was found that an ordinary 6-oz. Coca Cola bottle functioned excellently as a reaction vessel. This type of bottle conveniently fit the hydrogenation apparatus and could be easily and inexpensively procured. It readily withstood the hydrogen pressures employed (2-4 atmospheres) and was very resistant to breakage. Using

a Coca Cola bottle as the reaction vessel, the volume of the entire reaction system was found to be 0.2980 ± 0.0036 l.

The reaction bottle was encased in a metal jacket through which water from a constant temperature bath was circulated. The bath was maintained at $30.00 \pm 0.05^\circ$ for all hydrogenation runs. The rate of circulation of water to and from the bath was fast enough that the temperature drop was negligible. The reaction bottle was sealed to the rest of the system by means of a neoprene stopper which had previously been soaked in redistilled glacial acetic acid for 24 hours and then soaked overnight in distilled water. This treatment was designed to remove compounds which would poison the catalyst and spectrally contaminate the reaction mixture.

All pressure-time data were recorded on a Fischer-Porter automatic recorder which was connected to the hydrogenation apparatus. The pressure versus time curves were read directly to the nearest p.s.i.a. and estimated to the nearest 0.05 p.s.i.a. with the aid of a ruler and magnifying glass.

C. Hydrogenation Procedure

1. General

All glassware and spatulas which came in contact with catalyst, solvent, and reagents were very carefully cleaned. Reaction bottles were cleaned with chromic acid solution, washed three times with Sapolio, rinsed ten times with tap water, rinsed five times with distilled water, steamed with distilled water, and dried overnight in

an oven at 110-120°. Pipets and volumetric flasks were cleaned similarly with the omission of the washing with Sapolio and steaming.

All runs were carried out at a temperature of 30.0° and hydrogen pressures of 35-60 p.s.i.a. At least five minutes before each run was begun, water from the constant-temperature bath was allowed to circulate through the metal jacket and around the reaction bottle. Immediately before the reaction bottle was connected to the rest of the system at the beginning of a run, the inside of the metal connection to the bottle was cleaned with pipe cleaners, and the neoprene stopper was wiped with a Kleenex tissue. The pipe cleaner and Kleenex tissue had previously been dipped in redistilled glacial acetic acid. During the course of a run the temperatures of the room, hydrogenation apparatus, and constant-temperature bath were recorded. When not in use, the reaction system was always kept under hydrogen pressure. The hydrogenation runs were virtually always made in pairs.

2. Hydrogenation of Individual Hydrocarbons

In the hydrogenations of the individual hydrocarbons, 0.500 ml. of acceptor was used if the acceptor was a liquid; approximately 0.5 g. of acceptor was used if it was a solid. For benzene, toluene, and the xylenes the catalyst weights were 0.03 to 0.10 g.; for the less reactive polymethylbenzenes catalyst weights as large as 1.0 g. were employed. In each run 10.00 ml. of redistilled glacial acetic acid was used as solvent. All of the acceptors readily dissolved in the solvent except hexamethylbenzene, which is only sparingly soluble in glacial acetic acid. Fortunately, the solubility of hexamethylbenzene

was sufficient to permit the evaluation of its standard rate constant. At the beginning of each hydrogenation run the reaction system was alternately evacuated with a vacuum pump and filled five times with hydrogen before the run was initiated. Only pressure-time data were taken for the hydrogenations of the individual acceptors.

An important precaution which had to be observed in the hydrogenations of the individual acceptors was the establishment of equilibrium shaking (i.e., the experimental condition under which the effect of diffusion processes upon the rate of reduction is insignificant). This may be accomplished by showing that the experimental rate is directly proportional to the catalyst weight or independent of the rate of agitation of the reaction mixture. In this work two pulley wheels which agitated the reaction mixture at rates of 210 and 320 cycles per minute were used. Reduction rates in a Coca Cola bottle at the slow shaking rate (210 cycles/minute) varied slightly less than linearly with catalyst weight. In addition, the reduction rate was approximately 7 to 10 per cent slower at this shaking rate than at the faster one. At a shaking rate of 320 cycles per minute, the rate of reduction was in all cases directly proportional to the catalyst weight with the weight varying by a factor of two or more. It thus appears that equilibrium shaking was present for the faster rate of agitation, but not for the slower one. Therefore, all valid experimental data were taken at a shaking rate of 320 cycles per minute.

3. Binary Competitive Hydrogenations

Although the catalyst and experimental conditions for the competitive hydrogenations were the same as those used in the hydrogenations of the individual acceptors, certain experimental procedures were altered in carrying out the competitive runs. For any given set of competitive reductions (e.g., benzene versus toluene) it was imperative that the experimental procedure for every member of the set be precisely the same. This was necessitated by the nature of equation (43), which was used to correlate the experimental data. Every precaution was taken to enable this condition to be satisfied.

In most of the sets of competitive hydrogenations, a single stock solution of the two acceptors in redistilled glacial acetic acid was prepared. The concentrations of the two acceptors were approximately of the same magnitude (0.16-0.23 mole/l.). The low solubility of hexamethylbenzene required that the initial concentrations in its competitive reduction with pentamethylbenzene be approximately 0.075 mole/l. For each individual run, 10.00 ml. of this stock solution was pipetted into the reaction bottle. In a few of the sets of competitive reductions (those of benzene-toluene, benzene-para-xylene, toluene-para-xylene, and benzene-meta-xylene) the acceptors and solvent were added separately. For each of these runs 0.250 ml. of each acceptor and 9.50 ml. of solvent were added to the reaction bottle. This method of acceptor addition gave good experimental results; however, from a practical as well as a theoretical viewpoint, it is inferior to the use of a stock solution.

At the beginning of each competitive reduction the reaction system was alternately evacuated with a vacuum pump and filled three times with hydrogen before commencing the run. For a given set of reductions all of the evacuations were carried to the same low pressure (approximately 50 mm. mercury pressure) as read on a mercury manometer attached to the evacuation system. This procedure was followed to insure that the initial concentrations of the two acceptors were the same for each member of the set. Ignoring this procedure could lead to significant error in the competitive reduction of two acceptors with appreciably different vapor pressures.

As required by the use of equation (43), each set of competitive reductions was carried out with the same catalyst weight. This weight was always within the equilibrium shaking limit for both acceptors. As the competitive reduction proceeded, pressure-time data were recorded. At the end of each run a sample of the reaction mixture was diluted (usually 99:1) with undistilled glacial acetic acid in order to carry out the spectrophotometric analysis.

D. Spectrophotometric Analyses

1. Method and Apparatus

Acceptor concentrations of the reaction mixtures from the competitive hydrogenations were determined by ultraviolet absorption spectrophotometry. This analytical method was adapted from the work of Tunnicliff, Brattain, and Zumwalt.⁸⁹ It is based upon the fundamental assumption that the absorbancy of a mixture of acceptors is the

sum of the absorbancies which the individual acceptors would possess in the absence of each other. It also assumes that each acceptor obeys Beer's law (i.e., its absorbancy is proportional to its concentration).

For a beam of light entering a solution of an individual acceptor with intensity I_0 and leaving the solution with intensity I , the fundamental laws of colorimetry⁹⁰ reveal that,

$$\log \frac{I_0}{I} = a_s bc = A_s \quad , \quad (48)$$

where A_s is the absorbancy of the solution, a_s is the absorbancy index of the solute, and b and c are the length of solution through which the beam passes and acceptor concentration, respectively. Equation (48) assumes no absorption of radiation by the solvent. Using a known constant cell path, the absorbancy index of a given acceptor may be obtained from the slope of a plot of absorbancy versus concentration.

The method for the analysis of binary mixtures of acceptors embraces the measurement of the absorbancy of the mixture at two different wave lengths (λ and λ'). Thus, the analysis of acceptors A and B will depend upon the measurement of absorbancy (A) at wave length λ and absorbancy (A') at wave length λ' . If the absorbancy indexes of A and B are known at λ and λ' , the concentration of A (C_A) and the concentration of B (C_B) may be calculated from two simultaneous equations,

$$A = a_A C_A + a_B C_B \quad , \quad (49)$$

$$A' = a_A' C_A + a_B' C_B \quad , \quad (50)$$

where a_A and a_A' are the absorbancy indexes of A at λ and λ' , respectively,

and a_B and a_B' are the absorbancy indexes of B at λ and λ' , respectively. These equations may be rearranged to,

$$C_A = \frac{a_B' A - a_B A'}{a_A a_B' - a_A' a_B} \quad , \quad (51)$$

$$C_B = \frac{a_A A' - a_A' A}{a_A a_B' - a_A' a_B} \quad , \quad (52)$$

which are explicit expressions for C_A and C_B . An inspection of equations (51) and (52) reveals that λ and λ' should be chosen so that the absorbancy indexes of A differ as much as possible, and the absorbancy index of B is as small as possible at the wave length at which the absorbancy of index of A has its larger value and as large as possible at the wave length at which the absorbancy index of A has its smaller value.

All absorbancy measurements were made with a Beckman model DU quartz spectrophotometer. To permit the use of narrow slit widths, the 2000 megohm resistor in the grid circuit of the electrometer tube was replaced by a 10,000 megohm resistor. This replacement made the movements of the galvanometer much more sluggish; it thus increased the difficulty of zeroing the galvanometer. Thermospacers were placed on each side of the cell compartment to enable it to be kept at a constant temperature. Water from the constant-temperature bath (bath temperature, $30.0 \pm 0.1^\circ$) was circulated through the thermospacers. Measurements of cell-compartment temperature demonstrated that its maximum variation should have a negligible effect upon the absorbancy readings. The use of the thermospacers was necessitated by the large temperature coefficients (0.50-0.75 per cent per degree) of the

absorbancy indexes of the acceptors.⁹¹ All absorbancy data were taken in acetic acid solution with the use of matched quartz cuvettes of 1.00 cm. cell length.

2. Experimental Procedure

The success of the spectrophotometric method demanded that the reaction solutions remain spectrally uncontaminated during the course of the competitive reductions. Mock hydrogenation runs were carried out to determine the degree of this contamination. It was found that the preponderance of the contamination came from the stopper which was used to connect the reaction bottle to the rest of the reaction system. A neoprene stopper treated as described previously was found to produce the minimum amount of spectral contamination. In most of the mock runs the spectral contamination from the neoprene stoppers was found to be negligible when the dilution of the reaction mixture prior to the analysis was taken into consideration. In some of the mock runs of longer duration, 12 minutes or longer, the spectral contamination from the neoprene stopper was found to be capable of altering the analytical results by 1 to 3 per cent.

Since glacial acetic acid, the solvent used in the spectrophotometric analyses, also absorbs in the ultraviolet region of the spectrum, the absorption spectrum of the pure solvent was taken against a standard of triple-distilled water. This spectrum showed virtually complete absorption below 245 m μ . Above 260 m μ the absorption of the pure solvent was low enough to permit the galvanometer bridge of the instrument to be zeroed when the solvent was used as

the standard with a slit width of 0.200 mm. This narrow slit width was used because of the necessity of having a very thin band of radiation pass through the solution.⁸⁹

To reduce the error in reading the absorbancy (optical density) dial of the spectrophotometer, a minimum of three to five readings were taken for each absorbancy value. These readings were then averaged to obtain the absorbancy value. For each reading the absorbancy scale was kept covered until the galvanometer bridge was zeroed. It was then uncovered, and the reading was taken. The galvanometer scale was viewed through a magnifying glass. All absorbancy readings were taken with an independent wave length setting. All wave length settings were made from the short wave length side of the wave length scale.

Each absorbancy value was corrected for the difference between the absorption of the standard cuvette and that of the sample cuvette. This correction was made by taking the difference between the absorbancies of the sample and standard cuvettes containing sample and standard, respectively, at a predetermined wave length between 290 and 300 mμ. At this wave length no absorption resulted from the aromatic hydrocarbons under consideration. The use of numerous blank solutions of the same composition as the standard showed this correction to be valid at the wave lengths which were used in the analyses, 260-280 mμ. A new absorbancy correction was made for each individual value. All absorbancy values were taken with the cuvettes oriented in the same direction. The same cuvettes were always used for the sample and

standard, respectively. Undistilled reagent grade glacial acetic acid was used as the standard in all absorbancy determinations.

To assure that the solutions in the sample cuvette were at a constant temperature, they were immersed for a minimum of 30 minutes in the constant-temperature bath before being placed in the cuvette. After being placed in the cuvette, the sample was allowed to sit in the cell compartment of the instrument for a minimum of 10 minutes before any readings were taken.

The volumetric flasks and pipets used in this work were not calibrated. The flasks were listed as being accurate within 0.2-0.4 per cent; the pipets used in preparing the binary acceptor mixtures of known concentrations from the standard solutions were listed as being accurate within 0.2-0.4 per cent.⁹² Care was taken to see that all volumetric work was carried out when the room temperature was 22-25°.

3. Development of Analytical Method

The first step in the development of the analyses was the determination of the ultraviolet absorption spectra above 260 mμ of the acceptors in glacial acetic acid. These spectra were taken with either the Beckman model DU spectrophotometer or the Cary model M-114 recording spectrophotometer. Figure 2 gives the absorption spectra of benzene, toluene, and the xylenes in glacial acetic acid. The ultraviolet absorption spectra permitted the selection of the wave lengths to be used in the quantitative determinations. The primary criterion governing the selection of these wave lengths was the differences in

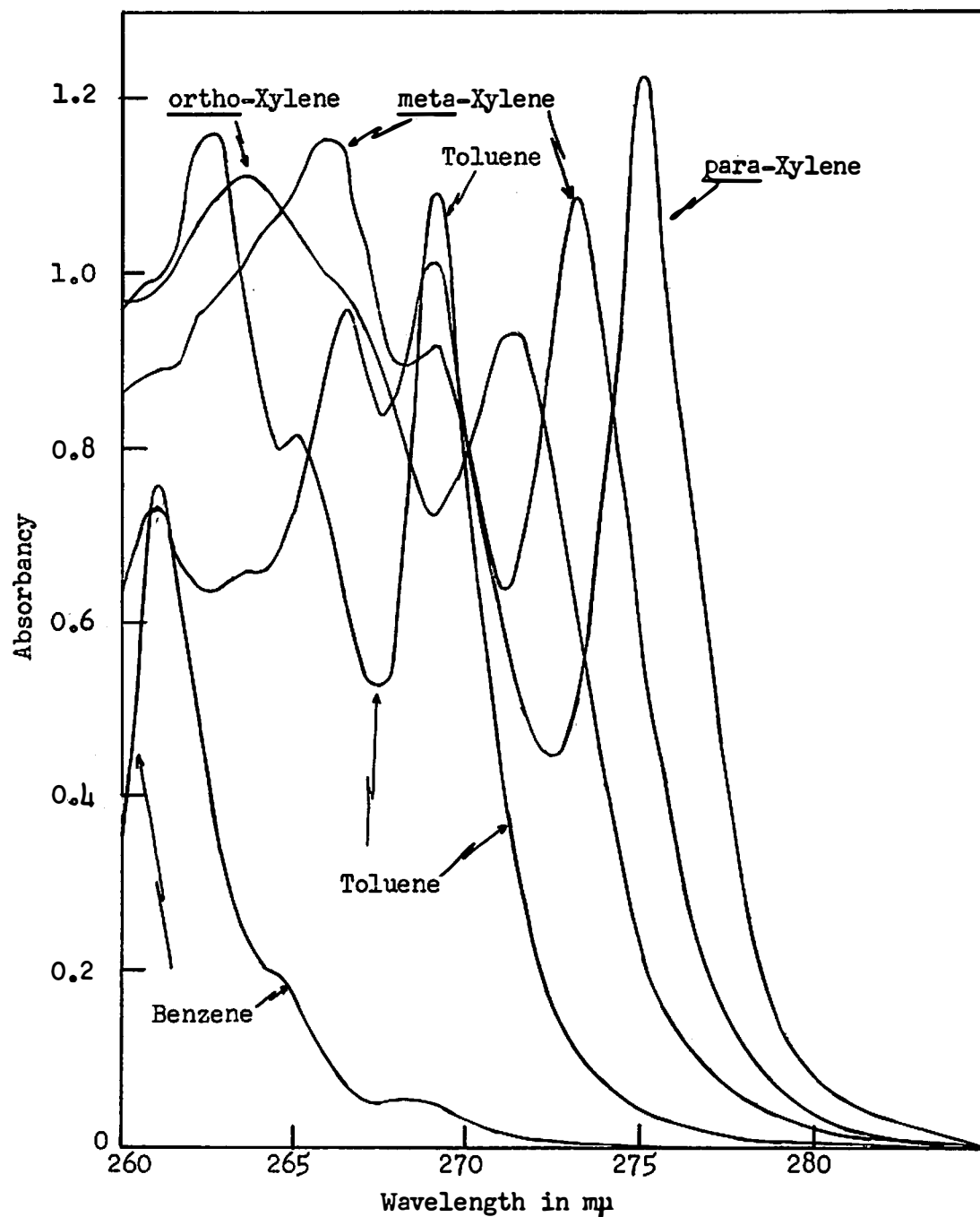


Figure 2. Ultraviolet adsorption spectra of benzene, toluene, and the xylenes in glacial acetic acid. Molar concentrations are benzene: 5.59×10^{-3} , toluene: 4.68×10^{-3} , p-xylene: 2.02×10^{-3} , m-xylene: 4.05×10^{-3} , and o-xylene: 4.13×10^{-3} .

absorbancy indexes discussed previously; the secondary criterion was the rate of variation of the absorbancy with wave length. It was desired to keep this rate of variation at a minimum in order that the absorbancy readings would not critically depend upon the wave length setting.

Following the selection of wave lengths, the absorption indexes were evaluated. A series of standard solutions of each acceptor was prepared. Absorbancy values of each solution were determined at each wave length to be used in the analyses of the binary mixtures of the acceptor. The absorbancy indexes were determined from the slopes of the plots of absorbancy versus concentration. In all cases an excellent linear relationship between absorbancy and concentration was observed. Within experimental error all of the plots passed through the origin. Figure 3 gives absorbancy-concentration plots for a series of standard meta-xylene solutions. A least-squares calculation was performed upon the absorbancy-concentration data in order to ascertain the best values for the absorbancy indexes.

4. Verification of Analytical Method

The spectrophotometric method of analysis was tested by analyzing binary acceptor mixtures of known concentrations. These mixtures were prepared by mixing in various proportions the standard solutions used in the absorbancy index determinations. All analyses were carried out soon after the calibrations were made in order to avoid error from the evaporation of the constituents of the solutions. The experimental procedure for all analyses was the same as that used

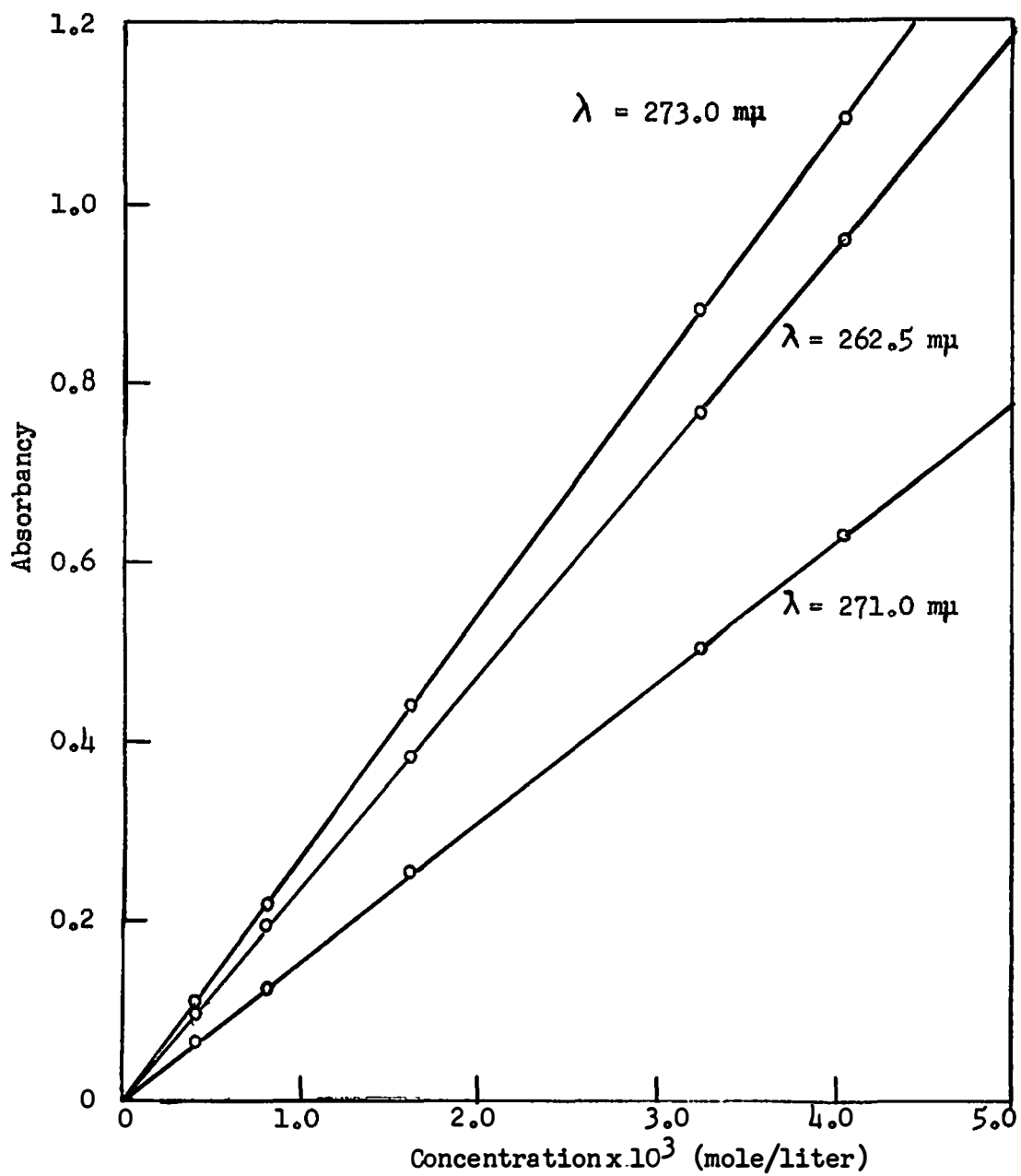


Figure 3. Plots of absorbancy versus concentration for a series of standard meta-xylene solutions.

in the absorbancy-index determinations. In this manner verification analyses were carried out for all pairs of acceptors which were hydrogenated competitively.

Table I gives the results of the verification analyses for the benzene-ortho-xylene mixtures. Wave lengths of 261.0 and 271.0 mμ were used. This series is typical of the mixtures which were analyzed. In this series as in all others five different solutions were analyzed.

Table II gives a summary of all of the verification analyses. The first two columns identify the solution constituents, A and B. The third column gives the two wave lengths which were used in the analyses. Columns four and five give the standard deviations of the per cent error in the analyses for constituents A and B. The standard deviations were calculated according to the formula,

$$\text{per cent standard deviation} = \pm \sqrt{\frac{\sum (d)^2}{n - 1}}, \quad (53)$$

where (d) is the absolute magnitude of the per cent deviation of an experimental concentration value from the true value, and n is the number of different analyses made in the same series. In this instance n is five.

An examination of Table II reveals that in virtually all cases the spectrophotometric method may be assumed to give reliable results within ± 3 per cent. The standard deviation for the pentamethylbenzene-hexamethylbenzene mixtures probably indicates a higher degree of accuracy than the method is actually capable of giving, since the spectra of the two hydrocarbons are so similar.

TABLE I
EXPERIMENTAL RESULTS OF THE ANALYSES OF BENZENE-ORTHO
XYLENE SOLUTIONS OF KNOWN CONCENTRATIONS

True Concentrations (mole/l. $\times 10^3$)		Concentrations from Analyses (mole/l. $\times 10^3$)		Percentage Error	
Benzene	<u>o</u> -Xylene	Benzene	<u>o</u> -Xylene	Benzene	<u>o</u> -Xylene
0.559	0.825	0.560	0.839	0.2	1.7
1.119	0.413	1.095	0.424	-2.1	2.7
1.398	1.650	1.405	1.657	0.5	0.4
2.237	2.063	2.183	2.073	-2.4	0.5
2.797	2.063	2.790	2.069	-0.2	0.3

TABLE II
SUMMARY OF RESULTS OF ANALYSES OF BINARY ACCEPTOR
SOLUTIONS OF KNOWN CONCENTRATIONS

Constituent A	Constituent B	Wave Lengths Used in Analyses (μ)	Standard Deviation of per cent Error for A	Standard Deviation of per cent Error for B
Benzene	Toluene	261.0 269.0	1.9	1.6
Benzene	<u>p</u> -Xylene	261.0 269.0	2.3	2.2
<u>p</u> -Xylene	<u>o</u> -Xylene	261.0 269.0	1.0	1.6
<u>p</u> -Xylene	<u>m</u> -Xylene	262.5 269.0	2.2	1.5
<u>o</u> -Xylene	<u>m</u> -Xylene	269.0 271.0	1.3	2.6
<u>p</u> -Xylene	Toluene	262.5 275.0	0.8	0.9
<u>m</u> -Xylene	Toluene	262.5 273.0	0.8	0.7
<u>o</u> -Xylene	Toluene	269.0 271.5	1.0	1.0
Benzene	<u>o</u> -Xylene	261.0 271.0	1.6	1.6
Benzene	<u>m</u> -Xylene	261.0 271.0	1.8	1.2
<u>p</u> -Xylene	Hemimellitene	262.5 275.0	0.5	2.3

TABLE II (CONTINUED)

Constituent A	Constituent B	Wave Lengths Used in Analyses (mμ)	Standard Deviation of per cent Error for A	Standard Deviation of per cent Error for B
p-Xylene	Mesitylene	272.0 275.0	1.6	2.8
Pseudocumene	Hemimellitene	262.5 276.0	0.2	0.7
Hemimellitene	Isodurene	262.0 277.5	1.2	1.0
Isodurene	Durene	266.0 273.5	2.8	1.8
Prehnitene	Durene	266.0 273.5	2.6	0.9
Prehnitene	Pentamethylbenzene	271.0 280.0	1.4	0.8
Hexamethylbenzene	Pentamethylbenzene	271.0 280.0	2.5	2.2

The accuracy of this analytical method is sufficient for analyzing the reaction mixtures from the competitive hydrogenations. These mixtures were analyzed in precisely the same manner as the solutions of known concentrations.

E. Treatment of Experimental Data

In the hydrogenations of the individual hydrocarbons only pressure-time data were taken. These data were used to evaluate the standard first-order rate constants. For the hydrogenation of a pure acceptor, A, equation (17) was a valid rate equation. This equation was integrated and arranged into the following form:

$$\log P = \frac{-k_A W_C t}{2.303 S V_S} + \log P_0, \quad (54)$$

where P_0 is the hydrogen pressure at zero reaction time. A plot of $\log P$ versus time yielded a straight line of slope $-k_A W_C / 2.303 S V_S$. The standard first-order rate constant was evaluated from the slope of this straight line. In many cases catalyst poisoning was observed. In these instances the slope for the early portion of the reaction was used for the evaluation of k_A . Figure 4 gives a plot of $\log P$ versus time for the reduction of para-xylene. The first two points lie above the line due to the reduction of the platinum oxide catalyst. The completion of the reduction is indicated by the plot becoming horizontal.

For the competitive hydrogenations both pressure-time and concentration data were taken. For each pair of acceptors which was hydrogenated competitively, a series of reductions was carried out using

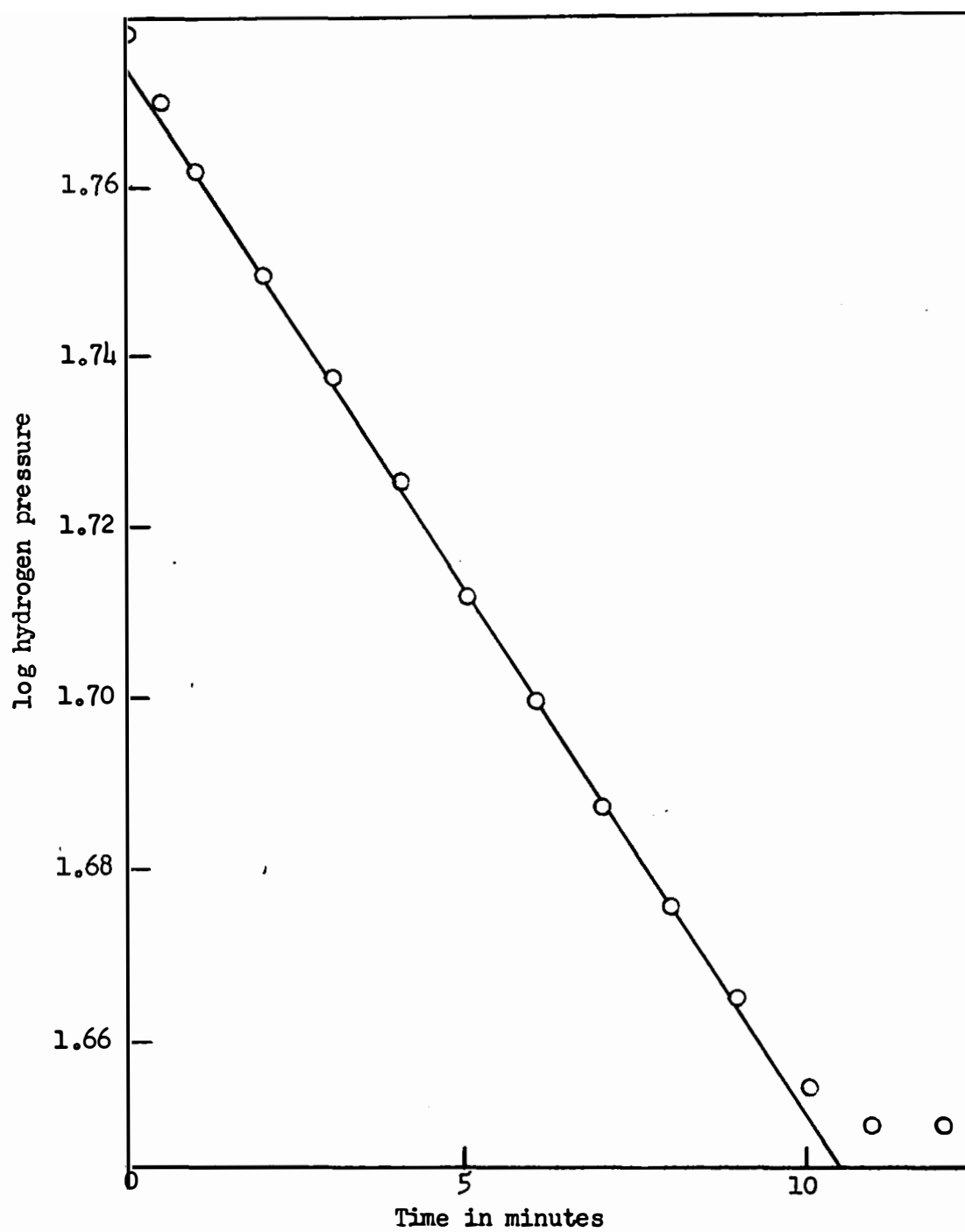


Figure 4. Plot of log hydrogen pressure versus time for hydrogenation of para-xylene.

the same catalyst weight and precisely the same procedure. These reductions were carried out to different degrees of completion in order to obtain simulated concentration data for a single competitive hydrogenation. Simulated concentration data for time zero of the reaction were obtained by carrying out a blank run in which no catalyst was used and analyzing the resulting reaction solution.

For a simulated competitive hydrogenation of acceptors A and B equation (43) may be applied,

$$\log C_A = \frac{k_A K_{AB}}{k_B} \log C_B + \left(\log C_A^0 - \frac{k_A K_{AB}}{k_B} \log C_B^0 \right) . \quad (43)$$

Plots were made of $\log C_A$ versus $\log C_B$ with the variation of at least one acceptor concentration being a minimum of an order of magnitude (except for the competitive reduction of pentamethylbenzene and hexamethylbenzene where the variation was a factor of three). In all cases well-defined straight lines were obtained. K_{AB} was evaluated by equating the slope of the plot to $k_A K_{AB}/k_B$. The best straight line was drawn through the experimental points. A least-squares calculation was not used because the increased accuracy which it would bring from the linear plots would be eclipsed by the uncertainty in k_A/k_B (approximately 8 per cent).

K_{AB} was evaluated from the pressure-time data for the binary reductions of benzene, toluene, and the xylenes. This evaluation was carried out by the use of equation (38). For a small finite reaction increment this equation may be altered to give,

$$K_{AB} = \frac{C_B}{C_A} \left[\frac{k_B + \frac{V_S S}{W_C P} \left(\frac{\Delta P}{\Delta t} \right)}{-k_A - \frac{V_S S}{W_C P} \left(\frac{\Delta P}{\Delta t} \right)} \right] . \quad (55)$$

The finite reaction period which is taken for the evaluation of K_{AB} is the period between reaction times of 1.00 and 2.00 minutes.

Several simulated runs in which no acceptor was used showed that with the catalyst weights used for benzene, toluene, and the xylenes all of the catalyst was reduced at the end of one minute reaction time. The selection of this increment of reaction should minimize the effects of catalyst poisoning upon the K_{AB} values.

The k_A and k_B values used in equation (55) were not obtained from the log P versus time plots. They were obtained by altering equation (17) to read,

$$k_A = - \frac{V_S S}{W_C P} \left(\frac{\Delta P}{\Delta t} \right) . \quad (56)$$

In equations (55) and (56) $\Delta P/\Delta t$ was taken as the pressure drop between reaction times 1.00 and 2.00 minutes for the reduction of pure A and for the reduction of a binary mixture of A and B. k_B was obtained in the same manner as k_A . C_A and C_B values were measured directly at a reaction time of 1.50 minutes for the competitive reductions. P was taken as the hydrogen pressure at this same time (1.50 minutes) in both the individual and competitive reductions. It should be remembered that the use of equation (55) for the evaluation of K_{AB} yields results which are decidedly inferior to those resulting from the concentration data. It does provide, however, an independent check of the K_{AB} values obtained from the concentration data.

CHAPTER IV

RESULTS

A. Hydrogenation of Individual Hydrocarbons

The evaluation of the data from the competitive hydrogenations required a knowledge of the relative rates of reduction of the acceptors being studied. The relative rates of reduction of benzene, toluene, and the polymethylbenzenes have been determined previously by Smith and Pennekamp.⁴⁶ For a valid quantitative evaluation of the data from the competitive hydrogenations, it was deemed necessary to redetermine the standard first-order rate constants of the acceptors under precisely the same experimental conditions as would be used in the competitive hydrogenations.

In Table III is given a comparison of the standard first-order rate constants from the log P versus time plots of this investigation with the rate constants obtained by Smith and Pennekamp.¹⁷ Both sets of rate constants show that as a general trend the rate constants decrease with increasing nuclear substitution. For a given set of isomers, the rate is observed to increase with symmetry of nuclear substitution. These two sets of rate constants are basically in mutual accord, although the absolute magnitudes of the two sets differ appreciably. With one exception their relative magnitudes are qualitatively the same. This exception is the relative reduction rates of durene (1,2,4,5-tetramethylbenzene) and isodurene (1,2,3,5-tetramethylbenzene).

TABLE III

COMPARISON OF STANDARD RATE CONSTANTS FOR THE
HYDROGENATION OF INDIVIDUAL HYDROCARBONS AT
30° WITH THOSE OBTAINED IN PREVIOUS WORK

Compound	This Investigation		Previous Work ^a	
	k g.-l ⁻¹ min.-l ⁻¹	Relative Rate	k g.-l ⁻¹ min.-l ⁻¹	Relative Rate
Benzene	0.2048	100	0.288	100
Toluene	0.1474	72	0.188	65
<u>ortho</u> -Xylene	0.0910	43	0.092	32
<u>meta</u> -Xylene	0.1258	61	0.142	49
<u>para</u> -Xylene	0.1576	77	0.186	65
Hemimellitene	0.0446	22	0.041	14.2
Pseudocumene	0.0894	43	0.084	29
Mesitylene	0.1486	72	0.166	58
Prehnitene	0.0239	11.7	0.028	9.7
Isodurene	0.0515	25	0.033	11.4
Durene	0.0508	25	0.052	18.0
Pentamethylbenzene	0.0153	7.5	0.010	3.5
Hexamethylbenzene	0.0029	1.4	0.0006	0.2

^aSee reference 17.

Contrary to the work of Smith and Pennekamp, this investigation has revealed that durene, the most symmetrically substituted tetramethylbenzene, is reduced at essentially the same rate as its isomer, isodurene. This is an apparent exception to the general rule of the reduction rate increasing as the symmetry of substitution increases.

In comparing the results of this investigation with those of Smith and Pennekamp, it should be remembered that the previous workers used their own preparation of Adams platinum oxide as catalyst; whereas, commercial platinum oxide catalyst was used in this work. This difference in catalysts can readily explain the observed differences in the absolute magnitudes of the standard rate constants.

Of greater concern, however, is the difference between the absolute magnitudes of the standard rate constants of the xylenes in this work and those in the precursor of this work.⁷¹ The relative rates of reduction are approximately the same in both investigations. The absolute magnitudes of the reduction rates differ, however, by as much as 35 per cent with the rate constants in the previous work being smaller in each case. In addition, the same type of catalyst was used in both investigations. It should be remembered that in each investigation equilibrium shaking was clearly shown to be present. Hence, the experimental kinetics were not affected by diffusion phenomena, and the kinetic data of both investigations may be considered valid. Moreover, the relative magnitudes of the rate constants are of appreciably greater interest than the absolute magnitudes.

These differences in rate constants may possibly be due to differences in catalyst poisoning by the rubber stopper connected to the bottles. A black rubber stopper was used in the previous research; a neoprene stopper was used in this work. The previous investigation was carried out using a "citrate of magnesia" shaker bottle, and this one was carried out with a Coca Cola bottle as the reaction vessel. In the shorter "citrate of magnesia" shaker bottle the reaction solution would splash against the stopper much more than in the taller Coca Cola bottle. This could result in a lower apparent rate of reduction in the shorter bottle as was observed experimentally. Another cause of these differences in relative reduction rates may be the change in activity which the catalyst undergoes during aging, since the two investigations were carried out approximately one year apart.

B. Competitive Hydrogenation of Benzene and Toluene

Benzene and toluene were the first two acceptors to be hydrogenated competitively. Table IV gives a summary of the experimental results from this series of reductions. Columns three and four give the acceptor concentrations (C_B for benzene and C_T for toluene) remaining at the end of the various runs. Column five gives the quantity, $(V_S/W_{CP}) (\Delta P/\Delta t)$, for the reaction increment between reaction times of 1.00 and 2.00 minutes. Between reaction times of 1.00 and 2.00 minutes for the reduction of the pure acceptors, this value was found to be $0.2166 \text{ g.}^{-1}\text{min.}^{-1}$ for benzene and $0.1671 \text{ g.}^{-1}\text{min.}^{-1}$ for toluene. In all of these hydrogenations the catalyst weight was 0.635 g.

TABLE IV

ACCEPTOR CONCENTRATION DATA FOR THE COMPETITIVE
HYDROGENATION OF BENZENE AND TOLUENE

Run Number	Reaction Time in Minutes	C _B in mole/l.	C _T in mole/l.	$\left(\frac{V_S S}{W_C P}\right) \left(\frac{\Delta P}{\Delta t}\right)$ in g. ⁻¹ min. ⁻¹ l.
261	0.00	0.2296	0.2184	--
262	0.00	0.2211	0.2204	--
275	1.50	0.2158	0.2077	--
276	1.50	0.1950	0.1995	--
277	1.50	0.2035	0.2012	--
278	1.50	0.1946	0.2012	--
265	3.00	0.1371	0.1666	0.1888
266	3.00	0.1568	0.1774	0.1818
267	3.00	0.1564	0.1791	0.1939
268	3.00	0.1617	0.1792	0.1880
269	6.00	0.1003	0.1352	0.1877
270	6.00	0.1033	0.1355	0.1942
271	9.00	0.0728	0.1145	0.1810
272	9.00	0.0608	0.1017	0.1932
273	12.00	0.0348	0.0751	0.1879
274	12.00	0.0437	0.0852	0.1813

An inspection of the concentration data reveals that benzene disappears more rapidly from the reaction mixture than toluene. An evaluation of K_{BT} , the competitive adsorption equilibrium constant, should determine if this faster rate of disappearance of benzene is due primarily to its intrinsic rate of reduction, the fraction of the active surface it occupies, or both of these effects. Figure 5 gives a plot of $\log C_B$ versus $\log C_T$ for this series of competitive reductions. The plot clearly verifies the theoretical prediction of a linear relationship between $\log C_B$ and $\log C_T$. K_{BT} was determined from the slope of the plot and found to have a value of 0.80 where,

$$K_{BT} = \frac{C_B C_T}{C_T C_B} \quad . \quad (57)$$

The pressure-time data of the competitive reductions of benzene and toluene were evaluated to yield a K_{BT} value of 1.19. This appears to differ somewhat from the concentration value of K_{BT} . An inspection of the method of calculation of the K_{BT} value from the pressure-time data reveals that the difference in the above K_{BT} values may result from an error of only 2.5 per cent in the average $(V_B S / W_C P) (\Delta P / \Delta t)$ value of the binary mixture. This is within the experimental error of reading $\Delta P / \Delta t$. Thus, the pressure-time data agree with the concentration data within experimental error.

It should be remembered that the K values from the pressure-time data are subject to much more experimental error than those from the concentration data. Therefore, it may be concluded that on the active spots of the surface benzene is slightly more strongly adsorbed than toluene. If the ring is adsorbed flatwise on the surface, the

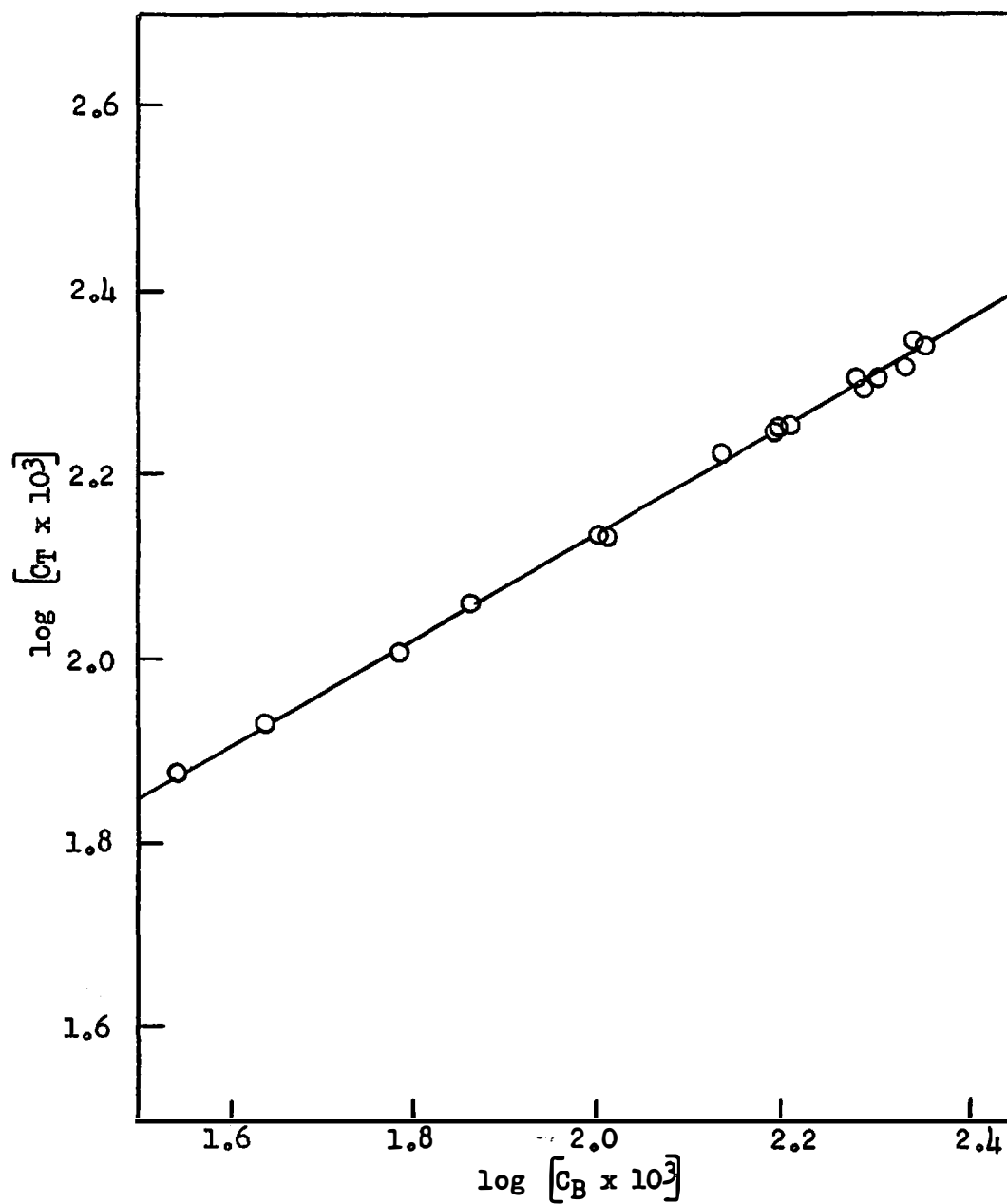


Figure 5. Plot of log toluene concentration (C_T) versus log benzene concentration (C_B) for the competitive hydrogenation of benzene and toluene.

slightly greater ease of adsorption of benzene may be attributed to the steric hindrance which the methyl group of toluene would present toward the adsorption of the ring on the catalyst surface. This steric hindrance would thus lower the strength of the bond(s) between the chemisorbed ring and the surface atoms of the catalyst.

C. Competitive Hydrogenation of Benzene with the Xylenes

Binary mixtures of benzene with each of the xylenes were reduced to determine the relative ease of adsorption of each acceptor on the catalytically active portion of the surface. All of the log-log plots of acceptor concentrations gave well-defined straight lines. Figure 6, which is a plot of $\log C_M$ versus $\log C_B$ for the competitive hydrogenation of meta-xylene and benzene, illustrates the linearity of these plots. Due to the relatively low concentration of benzene during the latter portion of the reaction, the probable error in the experimental points on the left side of the plot is appreciably greater than the error in the other points of the plot. The apparent deviation of the experimental points from the line during the reduction of the last few per cent of benzene may be attributed to experimental error in the C_B value.

The experimental data disclose that in all of the binary mixtures benzene was reduced much more rapidly than any of the xylenes. The determination of the competitive adsorption equilibrium constants should reveal if this rapid disappearance of benzene is due to its greater ease of adsorption as well as its greater intrinsic rate.

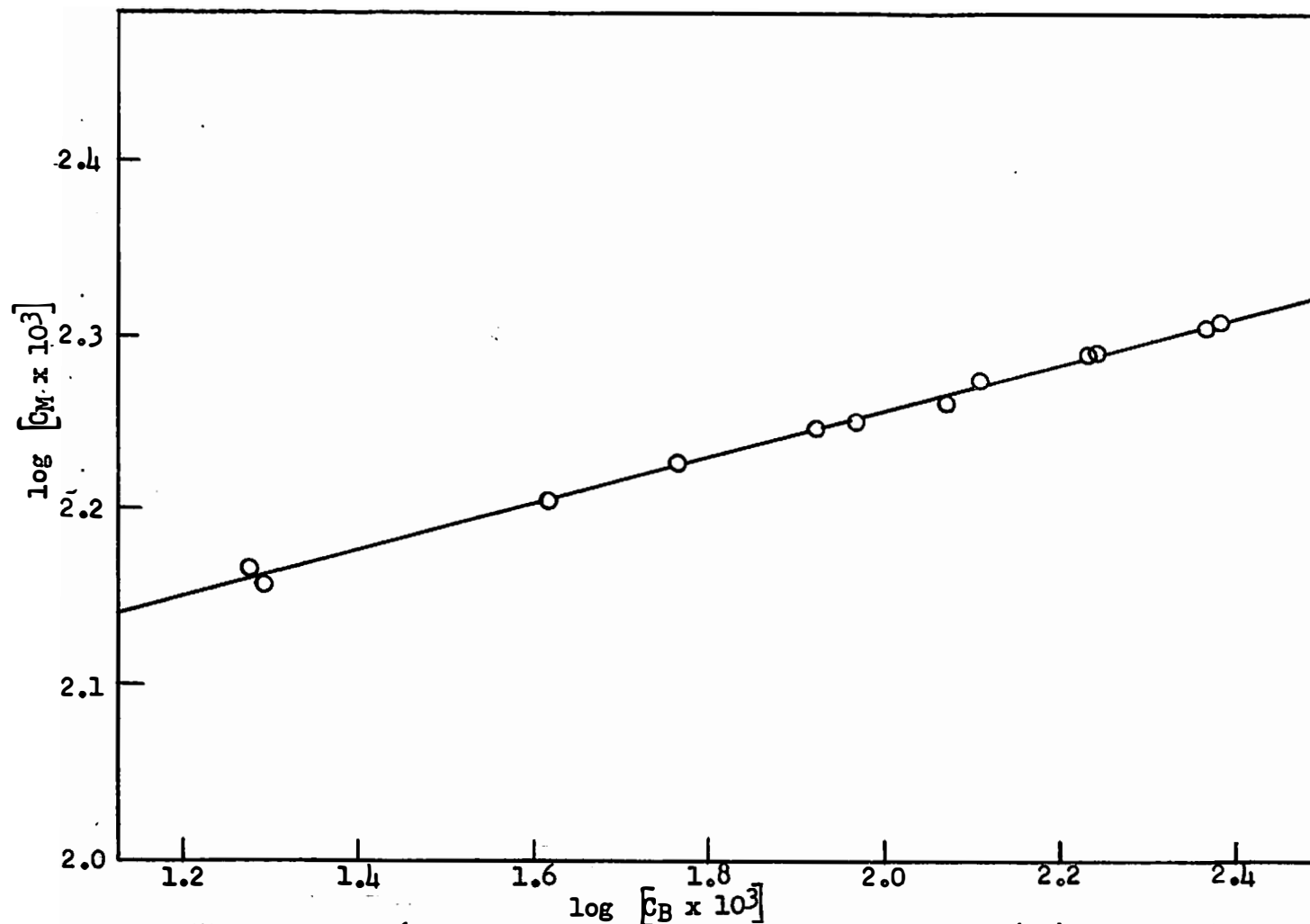


Figure 6. Plot of $\log$ meta-xylene concentration (C_M) versus $\log$ benzene concentration (C_B) for the competitive hydrogenation of meta-xylene and benzene.

In Table V are given the K values for the competitive reduction of benzene with each of the xylenes. Column two gives the catalyst weight which was used in each of the sets of binary reductions.

Table V reveals very satisfactory agreement between the concentration and pressure-time data. The two sets of K values are identical within the error which may be present in the pressure-time K values. These K values clearly show that benzene is much more strongly adsorbed on the active surface than any of the xylenes. A check of these competitive reductions with those between benzene and toluene reveals that the xylenes compete less effectively with benzene for the catalyst surface than does toluene. Thus, the additional methyl group of the xylenes increases the steric hindrance toward chemisorption of the ring if flatwise adsorption is assumed. As these data show, the introduction of the second methyl group into the ring apparently increases the steric hindrance to a greater extent than does the introduction of the first methyl group.

A further inspection of Table V reveals that ortho-xylene competes more effectively with benzene for the catalyst surface than does meta-xylene, which competes more effectively than para-xylene. From this it may be concluded that the relative ease of adsorption of the xylenes on the active surface decreases in the order of ortho, meta, para. This conclusion agrees with previous competitive hydrogenation studies of the xylenes.⁷¹

TABLE V
COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS FROM
THE COMPETITIVE HYDROGENATION OF BENZENE
WITH THE XYLENES

Xylene Being Competitively Reduced	Catalyst Weight (g.)	$K_{BX} = \frac{C_B \sigma_X^a}{C_X \sigma_B}$	
		From Concentration Data	From Pressure- time Data
<u>ortho</u> -Xylene	0.0776	0.335	0.438
<u>meta</u> -Xylene	0.0616	0.221	0.262
<u>para</u> -Xylene	0.0632	0.166	0.195

^aThe subscript X stands for the particular xylene under consideration.

D. Competitive Hydrogenation of Toluene and the Xylenes

Toluene was hydrogenated competitively against each of the xylenes in order to determine the relative effectiveness of the xylenes in competing with toluene for the catalyst surface. It was also desired to compare the effectiveness of the xylenes in competing against toluene with their effectiveness in competing against benzene. In each of the toluene-xylene reductions a well-defined linear plot of log toluene concentration versus log xylene concentration was obtained. Figure 7 gives the experimental log-log plot for the competitive reduction of toluene and meta-xylene. The experimental data again verify the existence of a linear variation between the logarithms of the acceptor concentrations.

In Table VI are given the competitive adsorption equilibrium constants which were obtained from the toluene-xylene hydrogenations. The second column gives the catalyst weight which was used in each set of hydrogenations. The agreement between the K values for the toluene-ortho-xylene reductions is much better than can be expected when the uncertainty involved in the pressure-time K value is considered. The difference between the K values for the toluene meta-xylene reductions is greater than a factor of two. This discrepancy can be rationalized by the fact that a 3 per cent variation in the $(V_S/W_C P) (\Delta P/\Delta t)$ value would cause the pressure-time K value to coincide with the concentration value. A 3 per cent variation is within the experimental error of reading $\Delta P/\Delta t$.

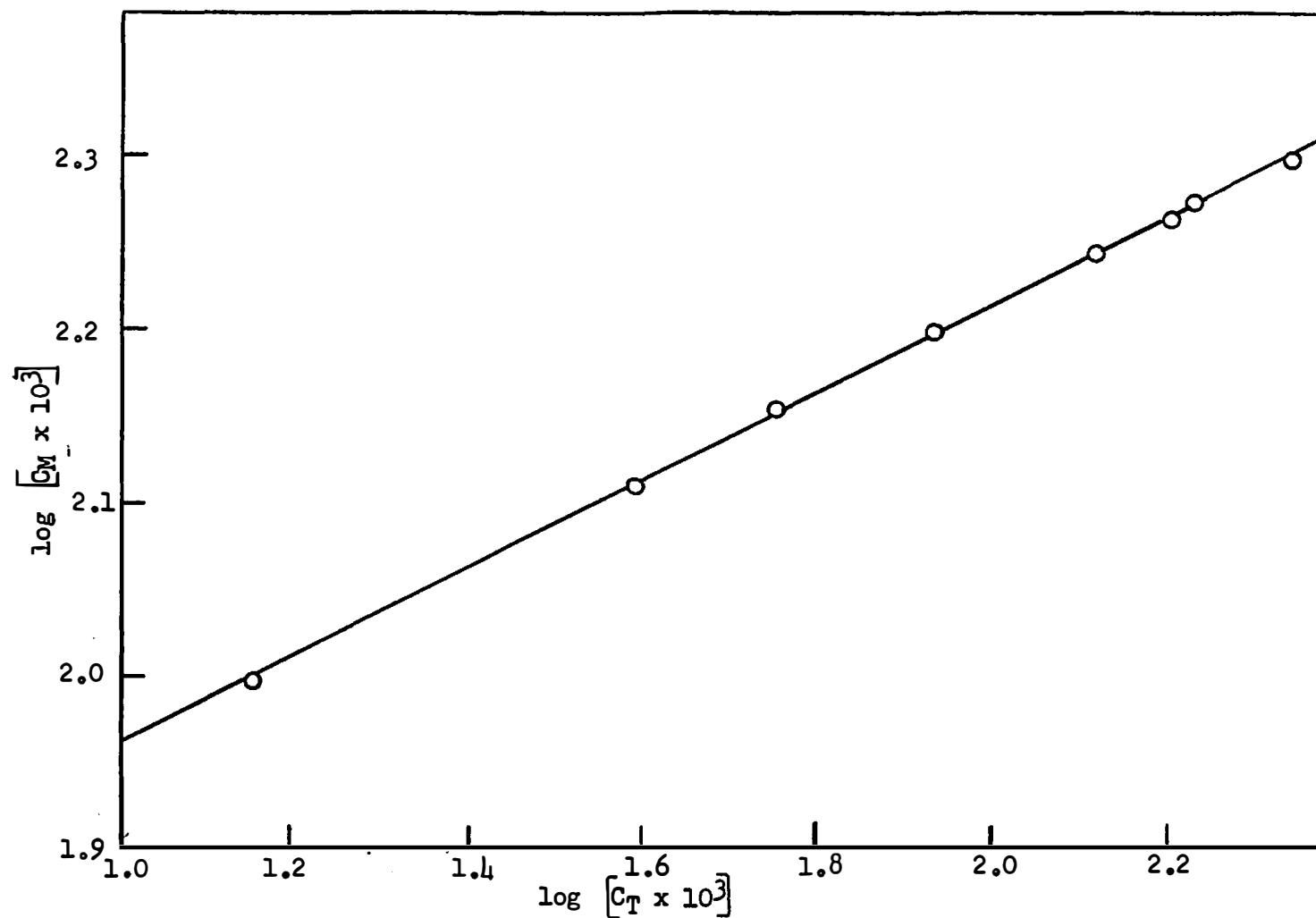


Figure 7. Plot of log meta-xylene concentration (C_M) versus log toluene concentration (C_T) for the competitive hydrogenation of meta-xylene and toluene.

TABLE VI
COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS FROM
THE COMPETITIVE HYDROGENATION OF TOLUENE
WITH THE XYLENES

Xylene Being Competitively Reduced	Catalyst Weight (g.)	$K_{TX} = \frac{C_T \sigma_X^a}{C_X \sigma_T}$	
		From Concentration Data	From Pressure- time Data
<u>ortho</u> -Xylene	0.0800	0.478	0.481
<u>meta</u> -Xylene	0.0700	0.294	0.701
<u>para</u> -Xylene	0.0645	0.246	--

^aThe subscript X stands for the particular xylene under consideration.

The K value for the competitive reduction of toluene and para-xylene was evaluated only from the concentration data. The close proximity of the standard first-order rate constants of toluene and para-xylene would render of little value an evaluation of K from the pressure-time data. It is of interest, however, that the average $(V_S/W_{CP}) (\Delta P/\Delta t)$ values for pure toluene, pure para-xylene, and their binary mixture are 0.1671, 0.1597, 0.1498 g.⁻¹min.⁻¹., respectively. The value for the binary mixture is outside the region between the two values of the pure acceptors. With respect to the mathematical analysis of the system, this result is absurd. It may be rationalized by considering the experimental error in each of the $(V_S/W_{CP}) (\Delta P/\Delta t)$ values and the possibility of more catalyst poisoning in the competitive reductions than in the reductions of the individual acceptors. Since the pressure-time K is obtained from the differences in the $(V_S/W_{CP}) (\Delta P/\Delta t)$ values, the experimental precision with which these values can be measured, as demonstrated above, is capable of producing a large amount of error in the pressure-time K.

A comparison of the K values from these sets of competitive reductions with those from the benzene-xylene reductions reveals that the xylenes compete for the catalyst surface more effectively against toluene than against benzene. This comparison is in agreement with the data from the competitive reduction of benzene and toluene which have revealed that benzene is slightly more strongly adsorbed than toluene. The results in Table VI clearly reveal that toluene is appreciably more strongly adsorbed on the active surface than any of the xylenes.

The K values in Table VI also disclose that the competition of the xylenes with toluene for the catalyst surface decreases in the order of ortho, meta, para. This finding agrees with the relative strengths of adsorption of the xylenes which were discovered in the benzene-xylene reductions and in the forerunner of this investigation.⁷¹ It provides more supporting evidence for the ease of adsorption of the xylenes decreasing with symmetry of substitution.

E. Competitive Hydrogenation of the Xylenes

The competitive reduction of the xylenes was carried out in order to measure directly their relative ease of adsorption. For each of the sets of competitive reductions, the log-log plot of acceptor concentrations gave an excellent straight line. Figure 8 gives the log-log plot for the competitive reduction of ortho-xylene and para-xylene.

The K values from the competitive reductions of the xylenes are summarized in Table VII. The pressure-time value of K for the para-xylene-meta-xylene reductions agrees excellently with the more accurately known concentration value. For the para-xylene-ortho-xylene reductions the two K values differ by a factor of approximately 1.8. This difference is not of much concern because it can result from an error of 6 per cent in the relative magnitudes of the $(V_g S / W_c P) (\Delta P / \Delta t)$ values of pure ortho-xylene and the binary mixture of ortho-xylene and para-xylene. The probability of such an experimental error is definitely appreciable. This discrepancy may also be partially due to the error in the $(V_g S / W_c P) (\Delta P / \Delta t)$ value for pure para-xylene. The excellent

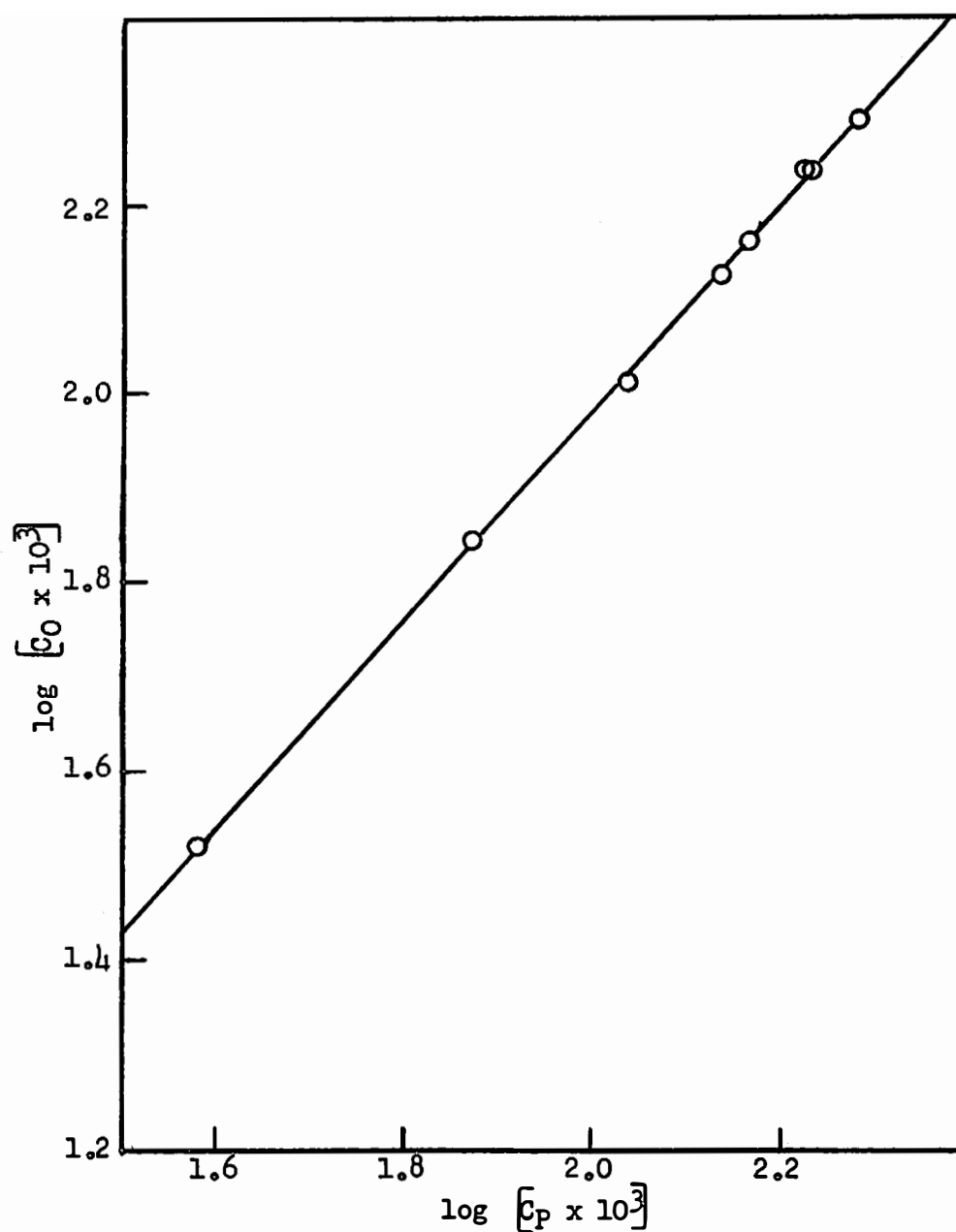


Figure 8. Plot of log ortho-xylene concentration (C_O) versus log para-xylene concentration (C_P) for the competitive hydrogenation of ortho-xylene and para-xylene.

TABLE VII
COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS FROM
THE COMPETITIVE HYDROGENATION OF THE XYLENES

Acceptors	Catalyst Weight (g.)	Definition	K^a	
			From Concentration Data	From Pressure- time Data
<u>para</u> -Xylene <u>meta</u> -Xylene	0.0800	$\frac{C_P \sigma_M}{C_M \sigma_P}$	1.24	1.41
<u>para</u> -Xylene <u>ortho</u> -Xylene	0.0800	$\frac{C_P \sigma_O}{C_O \sigma_P}$	1.90	3.36
<u>meta</u> -Xylene <u>ortho</u> -Xylene	0.0800	$\frac{C_M \sigma_O}{C_O \sigma_M}$	1.57	3.11

^aThe subscripts O, M, and P designate ortho-xylene, meta-xylene, and para-xylene, respectively.

linearity of the plot in Figure 8 tends to confirm the discrepancy in the K values as being due to the experimental error in determining K from the pressure-time data.

For the competitive reduction of meta-xylene and ortho-xylene the K values differ by a factor of two. This difference may result from an error of only 5 per cent in the relative magnitudes of the $(V_g S/W_c P) (\Delta P/\Delta t)$ values of pure ortho-xylene and the binary mixture of ortho-xylene and meta-xylene. The argument given for the discrepancy in the K values from the ortho-xylene-para-xylene hydrogenations is also valid in this case. Hence, the difference in the meta-xylene-ortho-xylene K values by a factor of two is not of serious concern.

The K values from the concentration data clearly show that the ease of adsorption of the xylenes on the active portion of the surface increases in the order of para, meta, ortho. This result agrees with the findings from the competitive reductions of benzene and toluene with the xylenes. In the precursor of this investigation⁷¹ the same conclusion was reached from the pressure-time data of the reduction of binary mixtures of the xylenes. Thus, there is good foundation for the statement that the relative ease of adsorption of the xylenes on the catalytically active portion of a platinum surface is the exact opposite of their relative rates of reduction.

As discussed in Chapter II, the experimental value of a given competitive adsorption equilibrium constant, K_{AB} , may be checked by competitively hydrogenating each acceptor against a third acceptor, C. Depending upon how K_{AB} , K_{AC} , and K_{BC} are defined, K_{AB} should be

obtained by an appropriate multiplication or division of K_{AC} and K_{BC} . In this work competitive hydrogenations have been carried out for all possible binary mixtures of benzene, toluene, and the xylenes. These sets of competitive reductions, ten in all, furnished four different, independent values for each competitive adsorption equilibrium constant. One of these values was determined by the direct competitive reduction of the two acceptors concerned. Each of the other three values was obtained by the competitive reduction of each of the two acceptors against a third acceptor.

In Table VIII is given a summary of the K values obtained from the reduction of the binary mixtures of benzene, toluene, and the xylenes. Each row contains the four experimental values of a given K. The first column gives the identity and definition of each K. The second column gives the value of K from the direct competitive reduction of the two acceptors concerned. The next three columns give the K values from the cross competitive hydrogenations with a third acceptor. They also show the method in which the K's of the cross competitive reductions are treated to obtain the desired K. All K values in Table VIII were obtained from the concentration data since the pressure-time K values contain a much larger percentage of error.

An inspection of Table VIII reveals that in each set of K values the agreement is within 10 per cent in most cases and within 20 per cent in all cases. This agreement is within the limits of experimental error. As the table indicates in a quantitative manner, the ease of adsorption of the five acceptors is,

TABLE VIII

SUMMARY OF THE EXPERIMENTAL VALUES OF THE COMPETITIVE ADSORPTION
EQUILIBRIUM CONSTANTS FROM THE COMPETITIVE HYDROGENATION
OF BENZENE, TOLUENE, AND THE XYLENES

K and Its Definition ^a	Direct Exptl. Value of K	Values of K as Determined from Other Sets of Competitive Hydrogenations			
$K_{BT} = \frac{C_B \sigma_T}{C_T \sigma_B}$	0.80	$\frac{K_{BO}}{K_{TO}} = 0.70$	$\frac{K_{BM}}{K_{TM}} = 0.75$	$\frac{K_{BP}}{K_{TP}} = 0.68$	
$K_{BO} = \frac{C_B \sigma_O}{C_O \sigma_B}$	0.335	$K_{TO} \times K_{BT} = 0.382$	$K_{BM} \times K_{MO} = 0.347$	$K_{BP} \times K_{PO} = 0.315$	
$K_{BM} = \frac{C_B \sigma_M}{C_M \sigma_B}$	0.221	$\frac{K_{BO}}{K_{MO}} = 0.213$	$K_{BT} \times K_{TM} = 0.235$	$K_{BP} \times K_{PM} = 0.206$	
$K_{BP} = \frac{C_B \sigma_P}{C_P \sigma_B}$	0.166	$K_{BT} \times K_{TP} = 0.197$	$\frac{K_{BO}}{K_{PO}} = 0.176$	$\frac{K_{BM}}{K_{PM}} = 0.178$	
$K_{TO} = \frac{C_T \sigma_O}{C_O \sigma_T}$	0.478	$\frac{K_{BO}}{K_{BT}} = 0.419$	$K_{TM} \times K_{MO} = 0.462$	$K_{TP} \times K_{OP} = 0.467$	
$K_{TM} = \frac{C_T \sigma_M}{C_M \sigma_T}$	0.294	$\frac{K_{BM}}{K_{BT}} = 0.276$	$\frac{K_{TO}}{K_{MO}} = 0.304$	$K_{TP} \times K_{MP} = 0.308$	

TABLE VIII (CONTINUED)

K and Its Definition ^a	Direct Exptl. Value of K	Values of K as Determined from Other Sets of Competitive Hydrogenations			
$K_{TP} = \frac{C_T \sigma_P}{C_P \sigma_T}$	0.246	$\frac{K_{BP}}{K_{BT}} = 0.208$	$\frac{K_{TO}}{K_{OP}} = 0.252$	$\frac{K_{TM}}{K_{MP}} = 0.237$	
$K_{OP} = \frac{C_P \sigma_O}{C_O \sigma_P}$	1.90	$\frac{K_{BO}}{K_{BP}} = 2.02$	$\frac{K_{TO}}{K_{TP}} = 1.94$	$K_{OM} \times K_{MP} = 1.95$	
$K_{OM} = \frac{C_M \sigma_O}{C_O \sigma_M}$	1.57	$\frac{K_{BO}}{K_{BM}} = 1.52$	$\frac{K_{TO}}{K_{TM}} = 1.63$	$\frac{K_{OP}}{K_{MP}} = 1.53$	
$K_{MP} = \frac{C_P \sigma_M}{C_M \sigma_P}$	1.24	$\frac{K_{BM}}{K_{BP}} = 1.33$	$\frac{K_{TM}}{K_{TP}} = 1.20$	$\frac{K_{OP}}{K_{OM}} = 1.21$	

^aThe subscripts B, T, P, M, and O are used to designate benzene, toluene, para-xylene, meta-xylene, and ortho-xylene, respectively.

benzene > toluene > ortho-xylene > meta-xylene > para-xylene .

It should be remembered that the relative reduction rates of these acceptors are,

benzene > toluene $\approx$ para-xylene > meta-xylene > ortho-xylene .

Thus, the relative reduction rate does not necessarily parallel the ease of adsorption.

The competitive reductions of benzene, toluene, and the xylenes were used as a critical experimental test of the theoretical treatment which was developed in Chapter II. The well-defined straight lines which were obtained in all of the log-log plots of acceptor concentrations attest to the correctness of this treatment. The fact that a log-log plot is not a very sensitive test of experimental data does not seriously detract from the significance of the linearity of the plots obtained in this work. The very satisfactory agreement of the K values in Table VIII provides another significant verification of the mathematical analysis. The agreement within experimental error of the K values from the concentration data with those from the pressure-time data fortifies the validity of this treatment. It may be concluded that the mathematical analysis of the competitive hydrogenation data has a very good experimental foundation.

F. Competitive Hydrogenation of the Trimethylbenzenes

The experimental verification of the theoretical treatment of the data from the binary competitive reductions permitted the

exploitation of this analysis in the determination of the relative ease of adsorption of the higher substituted polymethylbenzenes. In this exploitation K was evaluated only from the acceptor concentration data, although pressure-time data were taken. The linearity of a log-log plot of acceptor concentrations was regarded as evidence that the analysis was valid for the competitive reduction of the two acceptors under consideration.

The relative ease of adsorption of the trimethylbenzenes on the active surface was determined by competitively reducing para-xylene with mesitylene (1,3,5-trimethylbenzene), para-xylene with hemimellitene (1,2,3-trimethylbenzene), and hemimellitene with pseudocumene (1,2,4-trimethylbenzene). The use of para-xylene permitted a quantitative comparison of the relative ease of adsorption of the trimethylbenzenes with that of their lower homologs. Each of the log-log plots of acceptor concentrations yielded distinct straight lines. Figure 9 gives the plot for the reduction of the mixture of hemimellitene and pseudocumene. The plot for the para-xylene-hemimellitene reductions gave during the hydrogenation of the last fraction of para-xylene two points which deviated from the line by approximately the limit of experimental error. This apparent deviation showed the reduction of para-xylene to proceed at a greater relative rate than the linear plot would predict. This deviation is most likely due to experimental error. However, the possibility of para-xylene being reduced upon a small portion of the active surface which is unavailable for the reduction of hemimellitene should be noted.

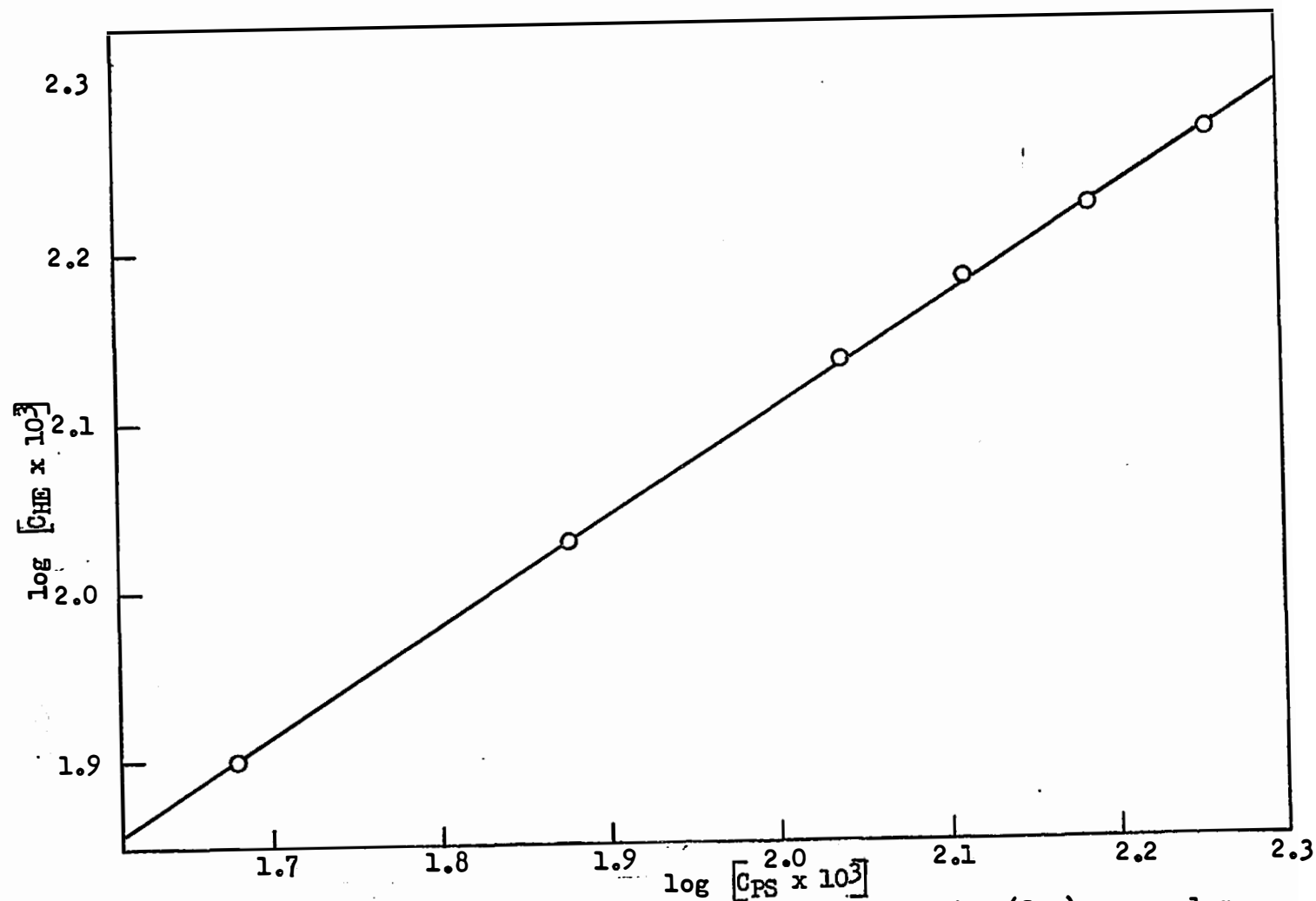


Figure 9. Plot of log hemimellitene concentration (C_{HE}) versus log pseudocumene concentration (C_{PS}) for the competitive catalytic hydrogenation of hemimellitene and pseudocumene.

Table IX gives the competitive adsorption equilibrium constants for the reduction of the trimethylbenzenes with para-xylene and with each other. The first column identifies the acceptors being reduced competitively, and the second column defines the K value given in column three. The last column states the method by which the K value was determined. Three of these were determined directly from the log-log plots of acceptor concentrations. The other three values were obtained by the appropriate multiplication or division of the three which were determined experimentally.

Table IX reveals that hemimellitene, the 1,2,3 isomer, is adsorbed with slightly greater ease than pseudocumene, the 1,2,4 isomer. Both pseudocumene and hemimellitene were adsorbed much more strongly than mesitylene, the 1,3,5 isomer. The relative ease of adsorption of the trimethylbenzenes on the active surface is,



This order is the exact reverse of the relative rates of reduction of the individual trimethylbenzenes. For the trimethylbenzenes the ease of adsorption decreases with increasing symmetry of substitution, but the relative reduction rate increases. This is the same effect as has been observed with the xylenes.

G. Competitive Hydrogenation of the Tetramethylbenzenes, Pentamethylbenzene, and Hexamethylbenzene

The tetramethylbenzenes, pentamethylbenzene, and hexamethylbenzene were reduced competitively to determine their relative ease of

TABLE IX
COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS
FOR THE COMPETITIVE HYDROGENATION
OF THE TRIMETHYLENZES

Acceptors	Definition ^a of K	K	Method of Obtaining K
para-Xylene Mesitylene	$\frac{C_{PX}\sigma_{ME}}{C_{ME}\sigma_{PX}}$	0.157	experiment
para-Xylene Pseudocumene	$\frac{C_{PX}\sigma_{PS}}{C_{PS}\sigma_{PX}}$	0.401	calculation
para-Xylene Hemimellitene	$\frac{C_{PX}\sigma_{HE}}{C_{HE}\sigma_{PX}}$	0.517	experiment
Hemimellitene Mesitylene	$\frac{C_{ME}\sigma_{HE}}{C_{HE}\sigma_{ME}}$	3.29	calculation
Hemimellitene Pseudocumene	$\frac{C_{PS}\sigma_{HE}}{C_{HE}\sigma_{PS}}$	1.29	experiment
Pseudocumene Mesitylene	$\frac{C_{ME}\sigma_{PS}}{C_{PS}\sigma_{ME}}$	2.55	calculation

^a The subscripts PX, ME, PS, and HE designate para-xylene, mesitylene, pseudocumene, and hemimellitene, respectively.

adsorption on the catalyst surface. The following pairs of acceptors were employed: hemimellitene-isodurene (1,2,3,5-tetramethylbenzene); isodurene-durene (1,2,4,5-tetramethylbenzene); durene-prehnitene (1,2,3,4-tetramethylbenzene); prehnitene-pentamethylbenzene; and pentamethylbenzene-hexamethylbenzene.

All of the log-log plots of acceptor concentrations were linear within experimental error. Figure 10 gives the plots for the isodurene-hemimellitene and prehnitene-pentamethylbenzene hydrogenations. The plot for the pentamethylbenzene-hexamethylbenzene reductions was more poorly defined than any of the others. This discrepancy may be rationalized by taking into consideration the relatively large experimental error in the analytical method of determining the acceptor concentrations. This error resulted from the very similar ultraviolet adsorption spectra of the two acceptors. Contamination from the neoprene stopper connected to the reaction bottle may also have caused appreciable experimental error in this case.

In Table X are given the K values for the reductions of the tetramethylbenzenes, pentamethylbenzene, and hexamethylbenzene. Column one identifies the two acceptors being reduced competitively. Column two defines the K value given in column three. Five of these values were obtained by direct experiment; the other four values were obtained by appropriate multiplication and division of these five.

The K values in Table X reveal that isodurene is slightly more strongly adsorbed than durene, and that prehnitene is appreciably more strongly adsorbed than either durene or isodurene. Thus, the relative

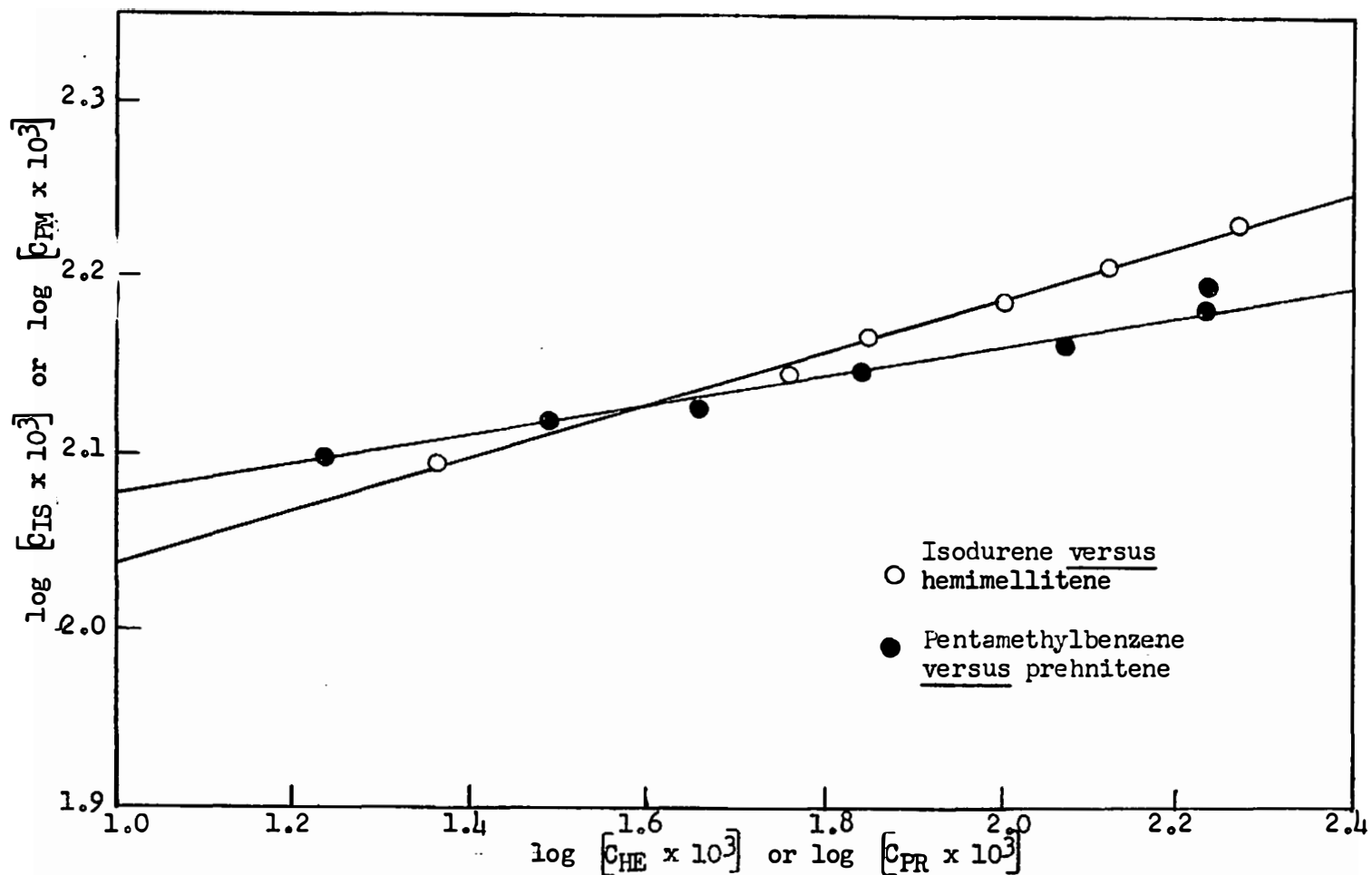


Figure 10. Plots of $\log$ isodurene concentration (C_{IS}) versus $\log$ hemimellitene concentration (C_{HE}) and $\log$ pentamethylbenzene concentration (C_{PM}) versus $\log$ prehnitene concentration (C_{PR}) for the competitive hydrogenations of isodurene versus hemimellitene and pentamethylbenzene versus prehnitene.

TABLE X

COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS FOR THE
COMPETITIVE HYDROGENATION OF THE TETRAMETHYLBENZENES,
PENTAMETHYLBENZENE, AND HEXAMETHYLBENZENE

Acceptors	Definition ^a of K	K	Method of Obtaining K
Hemimellitene Durene	$\frac{C_{HE}\sigma_{DU}}{C_{DU}\sigma_{HE}}$	0.111	calculation
Hemimellitene Isodurene	$\frac{C_{HE}\sigma_{IS}}{C_{IS}\sigma_{HE}}$	0.132	experiment
Hemimellitene Prehnitene	$\frac{C_{HE}\sigma_{PR}}{C_{PR}\sigma_{HE}}$	0.226	calculation
Prehnitene Durene	$\frac{C_{DU}\sigma_{PR}}{C_{PR}\sigma_{DU}}$	2.04	experiment
Prehnitene Isodurene	$\frac{C_{IS}\sigma_{PR}}{C_{PR}\sigma_{IS}}$	1.71	calculation
Isodurene Durene	$\frac{C_{DU}\sigma_{IS}}{C_{IS}\sigma_{DU}}$	1.19	experiment
Prehnitene Pentamethylbenzene	$\frac{C_{PR}\sigma_{FM}}{C_{FM}\sigma_{PR}}$	0.086	experiment
Prehnitene Hexamethylbenzene	$\frac{C_{PR}\sigma_{HM}}{C_{HM}\sigma_{PR}}$	0.122	calculation
Pentamethylbenzene Hexamethylbenzene	$\frac{C_{PM}\sigma_{HM}}{C_{HM}\sigma_{PM}}$	1.42	experiment

^aThe subscripts HE, PR, DU, IS, FM, and HM designate hemimellitene, prehnitene, durene, isodurene, pentamethylbenzene, and hexamethylbenzene, respectively.

ease of adsorption of the tetramethylbenzenes on the active surface is,



although the relative rates of reduction were found to be,



Again it is seen that increasing the symmetry of substitution for an isomeric set of polymethylbenzenes hinders the ease of adsorption. For the tetramethylbenzenes an increase in the symmetry of substitution will increase the reduction rate except in the case of isodurene and durene where the rates are identical within experimental error.

Table X reveals that pentamethylbenzene and hexamethylbenzene are much more weakly adsorbed on the surface than any of the tetramethylbenzenes. A surprising result, however, is that hexamethylbenzene appears to be more strongly adsorbed than pentamethylbenzene. It is highly improbable that the experimental error in the K value for the competitive reduction of these acceptors is sufficient to alter this result qualitatively.

CHAPTER V

INTERPRETATIONS AND CONCLUSIONS

A. General Interpretation

The results disclosed in the preceding chapter have demonstrated the validity and usefulness of a new method of measuring the ease of adsorption of benzene and its derivatives upon the active portion of a catalyst surface. As previously stated, this method is centered around the experimental determination of the competitive adsorption equilibrium constant, K , which is a direct measure of the relative ease of adsorption. It is not surprising, therefore, that the main experimental and theoretical effort of this work was directed toward more accurate and more reliable methods of evaluating K .

In a previous investigation of the author⁷¹ the K values were measured by taking the initial slope of the first-order kinetics plot ($\log P$ versus time) of a binary competitive reduction and evaluating from it a standard competitive rate constant, k_{AB} , which is not a true constant. The K value was then evaluated by comparing k_{AB} with the standard rate constants of the individual acceptors. This method provided K values which showed that the relative ease of adsorption of the xylenes on the active platinum surface is the exact reverse of their relative rates of reduction, a result which has been confirmed by this investigation. Also in the previous work an equation was derived

(q.v., equation (32) of this thesis) which predicted an increase in the slope of the log P versus time plots for the binary competitive hydrogenations of the xylenes. Such an increase in the slope was observed experimentally. The K values from this previous investigation were found to be accurate only within a factor of approximately two due to the magnification of the experimental error of the rate constants in the competitive adsorption equilibrium constants.

The method by which the K values were determined from the pressure-time data of this work (q.v., equation (38)) is scarcely better than the one mentioned above. Its one advantage is that the acceptor concentrations were measured directly; whereas, in the previous method the acceptor concentrations were assumed to be those which were present initially in the reaction mixture. Considering the evacuations which were carried out prior to each run, the method used for evaluating K in the previous work is inferior to the one employed in this investigation when acceptors of greatly different volatility (e.g., benzene and para-xylene) are competitively reduced. For the competitive reduction of the xylenes, which have virtually identical vapor pressures, the two pressure-time methods should yield results with comparable amounts of experimental error. Thus, the error in the pressure time K's of this research is such that an experimental value may differ from the true value by as much as a factor of two.

As the experimental data of this work have shown, the log-log plots of acceptor concentrations have yielded K values which are decidedly superior to those from the pressure-time data. The results verify

that the K 's obtained by this method may be considered as being accurate within 10 to 12 per cent with the possible exception of the value from the hexamethylbenzene-pentamethylbenzene reductions. With this single exception the linearity of the log-log plots was so well-defined that the main source of error arose from the ratio of the standard rate constants. It should be remembered that the use of acceptor concentration data for the evaluation of competitive adsorption equilibrium constants depends upon the employment of a suitable analytical method for the determination of acceptor concentrations. The accuracy of the analytical method critically affects the linearity of the log-log plots and the error in K . For this reason a substantial portion of this research was devoted to developing a method for the analysis of the binary acceptor mixtures in glacial acetic acid.

Two of the cardinal virtues of the theoretical treatment of the experimental data of this research are its simplicity and its foundation upon Langmuir kinetics. This treatment is fundamentally quite similar to that used by Wauquier and Jungers⁷⁰ in studying the relative ease of adsorption of benzene and its homologs on Raney nickel. Its simplicity is attested by the ease with which the experimental data may be correlated and treated mathematically to obtain the competitive adsorption equilibrium constants. Its foundation upon Langmuir kinetics enables this study to be related to the wealth of theoretical knowledge which is valid for surface reactions obeying these kinetics. The excellent agreement of the mathematical analysis with the experimental data indicates

that the active platinum surface upon which the acceptor is adsorbed is homogeneous at least to a first approximation. It is well to remember that the method of evaluating K from the acceptor concentration data requires only that the two acceptors obey Langmuir kinetics and are reduced according to the same form of rate equation. The kinetic necessity of this has been discussed by Jungers and Balaceanu.⁹³ The determination of K from the pressure-time data required an additional assumption of complete surface coverage by the acceptors.

The most valuable use of the K values obtained in this work is that of relating the ease of adsorption of the various acceptors to their relative reduction rates and molecular structure. It has been suggested that the effect of nuclear substitution upon the reduction rate of the benzene nucleus may be due to steric hindrance between the catalyst and the adsorbed molecule.⁹⁴ This question should be answered by the K values since their magnitudes should provide a measure of the relative amount of steric strain resulting from the adsorption of the various acceptors upon the catalytically active portion of the surface. A comparison of the relative reduction rates with the ease of adsorption should yield a more distinct picture of the interrelationship between the mode of adsorption of the benzene nucleus and the mechanism by which it is hydrogenated.

B. Relation between Molecular Structure, Ease of Adsorption,
and Reduction Rate

The results of this investigation have shown that the ease of adsorption of benzene and its derivatives does not necessarily parallel their rates of reduction. These results are summarized in Table XI, which gives the competitive adsorption equilibrium constants for the competitive reduction with benzene of each of the other aromatic hydrocarbons studied. The acceptors are listed in the order of their decreasing ease of adsorption. The first four K's were determined by experiment; the other values were obtained by appropriate multiplication or division of the experimental K's. Column three gives the relative reduction rates of the pure acceptors.

The ease of adsorption is observed to decrease as additional methyl groups are substituted onto the ring except in the case of hexamethylbenzene where it is observed to increase slightly. This effect is paralleled, in general, by the reduction rate, with the exception of pentamethylbenzene being reduced five times as rapidly as hexamethylbenzene. The relative ease of adsorption of these acceptors may be explained by assuming that the ring is adsorbed with its six π electrons forming weak chemical bonds with the surface atoms of the platinum catalyst. There is good experimental evidence that such is the case.^{35,94,95} This mode of adsorption means that the ring must either be adsorbed flatwise or at an angle with the surface which is small enough to permit significant interaction between the six π electrons and the surface atoms.

TABLE XI

A COMPARISON OF RELATIVE REDUCTION RATES WITH THE
COMPETITIVE ADSORPTION EQUILIBRIUM CONSTANTS
FOR THE COMPETITIVE HYDROGENATION OF
TOLUENE AND THE POLYMETHYLBENZENES
WITH BENZENE

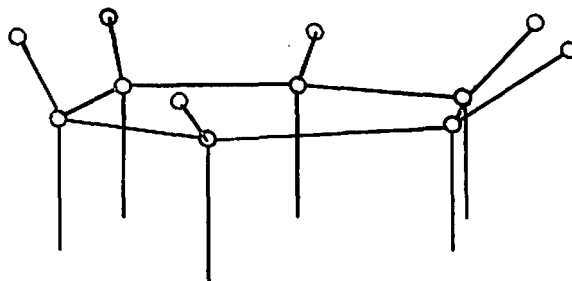
Acceptor (A)	$K_{AB} = \frac{C_B \sigma_A^a}{C_A \sigma_B}$	Reduction Rate Relative to That of Benzene
Toluene	0.80	0.72
<u>ortho</u> -Xylene	0.335	0.43
<u>meta</u> -Xylene	0.221	0.61
<u>para</u> -Xylene	0.166	0.77
Hemimellitene (1,2,3-trimethylbenzene)	0.086	0.22
Pseudocumene (1,2,4-trimethylbenzene)	0.067	0.43
Mesitylene (1,3,5-trimethylbenzene)	0.0261	0.72
Prehnitene (1,2,3,4-tetramethylbenzene)	0.0194	0.117
Isodurene (1,2,3,5-tetramethylbenzene)	0.0113	0.25
Durene (1,2,4,5-tetramethylbenzene)	0.0095	0.25
Hexamethylbenzene	0.0024	0.014
Pentamethylbenzene	0.0017	0.075

^aThe subscript A designates the acceptor which is being competitively hydrogenated with benzene.

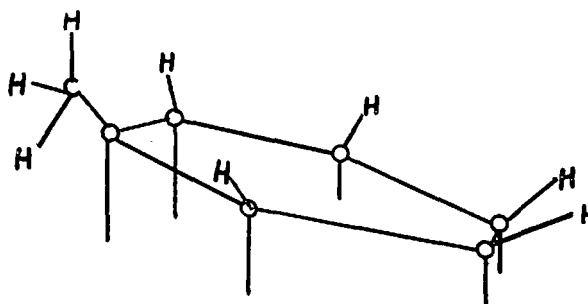
Upon adsorption the ring may well present the type of picture shown in Figure 11a in which the groups attached to the ring are pushed to the side opposite the catalyst surface. It is difficult to assess the degree to which the six carbon atoms of the ring depart from planarity. This departure cannot be very great for six point attachment of the ring to take place.^{35,95} As the bulk of the groups attached to the ring increases, the repulsion of these groups away from the catalyst surface will increase, and the strength of the bonds between the ring and the surface atoms will decrease. This is a frontal or F type of strain.

Another type of steric strain will develop by virtue of the nuclear substituents being pushed to the side of the ring opposite the catalyst. This effect will bring the substituents within closer proximity of each other. As the bulk of these substituents is increased, their mutual repulsion will increase, and the energy level of the adsorbed species will rise. Hence, the ease of adsorption will decrease as a result of this back or B type of strain. B strain is most important for substituents which are either ortho or meta to each other.

It is thus seen that increasing the bulk of the nuclear substituents such as exchanging a hydrogen atom for a methyl group will decrease the ease of adsorption as a result of both F and B strain. The experimental data reveal such a decrease. The introduction of the first methyl group to give toluene causes a slight but significant decrease in the ease of adsorption. A much greater decrease in the ease of adsorption results from the introduction of the second methyl



(a)



(b)

Figure 11. Postulated mode of chemisorption of the benzene nucleus. Illustration (a) depicts the benzene nucleus chemisorbed on the active surface; illustration (b) depicts the chemisorption of toluene. .

group into the ring than from the first. As the experimental results have shown, the ease of adsorption of the xylenes in comparison to toluene is much less than the ease of adsorption of toluene in comparison to benzene. In the cases of ortho and meta xylene the concept of B strain may be used to rationalize this result. For the adsorption of toluene the lone methyl group will have five hydrogen atoms with which to interact on the side of the ring opposite the catalyst surface. For the adsorption of the xylenes each methyl group will have four hydrogen atoms and another methyl group with which to interact. The hydrogen-hydrogen interactions may be considered as being much smaller than either the methyl-hydrogen or methyl-methyl interaction. The methyl-hydrogen and the methyl-methyl interactions of the xylenes produce a larger amount of B strain than the interaction between the lone methyl group of toluene and the five nuclear hydrogens.

The above rationalization appears to be adequate for the adsorption of ortho and meta-xylene. It does not appear sufficient, however, to explain the ease of adsorption of para-xylene with respect to that of toluene and benzene. In this case the two methyl groups will be too far apart to have significant mutual repulsion upon adsorption. The case of para-xylene can be understood if it is assumed that the ring may be tilted upon adsorption. For the chemisorption of toluene the ring will be tilted upon the side opposite the methyl group coming into more intimate contact with the surface (q.v., Figure 11b). This side of the ring will be bound to the surface more strongly than the side on which the methyl group is located. For the adsorption of para-xylene, however,

this type of tilted adsorption cannot occur since methyl groups are on both sides of the ring. It is conceivable that the ring of para-xylene can be adsorbed by being tilted about an axis passing through the two carbon atoms to which the two methyl groups are attached. This type of contact with the surface is definitely less intimate than the contact of the unsubstituted side of the ring of toluene. Hence, the bonding strength is decreased by an amount which is greater than that resulting from the introduction of the first methyl group. The concept of inclined adsorption of the ring may complement B strain in explaining the relative ease of adsorption of meta-xylene, toluene, and benzene.

The greatest argument for the presence of tilted adsorption of the ring arises from the comparison of the relative ease of adsorption of each of the three sets of substitutional isomers studied in this research. For the dimethylbenzenes, trimethylbenzenes, and tetramethylbenzenes the ease of adsorption decreased with increasing symmetry of substitution, although the effect of this symmetry upon the reduction rate was in the opposite direction. Thus, for the xylenes the ease of adsorption was,



This ease of adsorption cannot be explained by consideration of B strain since this effect would predict the ease of adsorption to be in the opposite direction. F strain by itself is also inept in explaining this phenomenon.

Inclined adsorption of the ring permits a ready rationalization of the above experimental facts. The adsorption of ortho-xylene will

present a picture which is quite similar to that resulting from the adsorption of toluene. The ring will be inclined with the side opposite the two methyl groups being closer to the surface. With meta-xylene a decreased amount of inclination takes place; with para-xylene it is even less. Thus, the intimacy of opposite-side approach decreases in the order of ortho-xylene, meta-xylene, para-xylene. This decrease manifests itself in the relative ease of adsorption of the xylenes which is experimentally observed. The same type of argument may be used to explain the relative ease of adsorption of the trimethylbenzenes and the tetramethylbenzenes. With each set of isomers a decrease in the symmetry of substitution will result in increased opportunity for tilted absorption of the ring which yields a greater ease of adsorption.

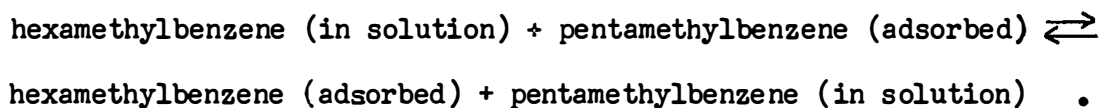
Further support for the idea of inclined adsorption of the ring may be obtained by comparing various homologous series of the polymethylbenzenes. The experimental data reveal that meta-xylene has a strength of adsorption which is greater than that of mesitylene (1,3,5-trimethylbenzene) by approximately an order of magnitude as measured by the K values in Table XI. Some of this decrease in the ease of adsorption is, of course, due to increases in B and F strain. A sizeable portion of it is most likely due to opportunity for inclined adsorption in meta-xylene and the virtual lack of it in mesitylene. If another methyl group is added to mesitylene to form isodurene, the decrease in ease of adsorption will this time be only a factor of two. This decrease may be reasonably explained by the presence of increased steric strain. Scale molecular models reveal that mesitylene and isodurene have approximately the same opportunity for inclined adsorption of the ring.

A comparison of the concepts of F strain and tilted adsorption discloses a very close relationship between them. The tendency or opportunity for inclined adsorption is a result of unsymmetrical F strain. It thus follows that inclined adsorption of the ring will decrease as the symmetry of substitution is increased. The inclination of the chemisorbed ring with respect to the surface may be regarded as a means of minimizing F strain.

With one exception all of the relative strengths of adsorption obtained in this work may be explained by the concepts of F strain, B strain, and inclined adsorption of the ring. This exception is the relative strengths of adsorption of pentamethylbenzene and hexamethylbenzene. The experimental results have disclosed, quite surprisingly, that hexamethylbenzene appears to be slightly more strongly adsorbed than pentamethylbenzene. This result may conceivably be explained on the basis of the statistical mechanical theory of equilibrium constants. According to this theory,⁹⁶ the competitive adsorption equilibrium constant as defined for this pair of acceptors will be directly proportional to the symmetry number of hexamethylbenzene in solution and inversely proportional to the symmetry number of the adsorbed species. It will likewise be directly proportional to the symmetry number of chemisorbed pentamethylbenzene and inversely proportional to the symmetry number of this acceptor in solution. The symmetry number is defined as the number of different but indistinguishable configurations which a given species may assume in space. If it is assumed that the symmetry of the ring of hexamethylbenzene is destroyed upon chemisorption, its abnormal strength of adsorption may be understood.

There are several misgivings to this statistical mechanical explanation. It does not agree with mesitylene being more weakly absorbed than any of its isomers. It also does not agree with benzene being but slightly more strongly absorbed than toluene. It seems that if the statistical mechanical interpretation were valid, benzene would be much more strongly absorbed relative to toluene than the experimental results show. In addition, the concept of the symmetry of the ring being destroyed upon adsorption does not appear to be compatible with the planar or approximately planar configuration of the chemisorbed ring discussed previously.

A more logical explanation for the surprisingly high ease of adsorption of hexamethylbenzene relative to pentamethylbenzene rests in the relative solubilities of the two acceptors in the solvent, glacial acetic acid. It should be remembered that the competitive adsorption equilibrium constant, K , was defined according to the reaction,



Any effect which would alter the relative chemical potentials (μ) of the two acceptors in solution should alter the experimental value of K . It is reasonable to expect such an effect to result from large differences in acceptor solubilities. Pentamethylbenzene was found to be much more soluble than hexamethylbenzene in glacial acetic acid. The mixture of these acceptors which was reduced competitively was virtually saturated with hexamethylbenzene; whereas, the concentration of pentamethylbenzene was far below the saturation point. It is logical to believe that a

solvent effect will increase the chemical potential of hexamethylbenzene relative to that of pentamethylbenzene. This effect will result in a greater thermodynamic driving force for the adsorption of hexamethylbenzene relative to that of pentamethylbenzene than would exist in the absence of the solvent. This driving force will result in an experimental value of the relative ease of adsorption of hexamethylbenzene which is greater than the true value which is solvent independent. The validity of this explanation could be ascertained by hydrogenating competitively these two acceptors in various other solvents.

At first consideration the effect of solvent upon the other K values of this research is cause for concern. This concern is readily dispelled by taking into account the close similarity of the molecular structure of all of the acceptors and, most important, the very large solubility which all of them have in glacial acetic acid and the relatively dilute solutions which were used in this work. This conclusion is corroborated by the work of Jungers and Wauquier,⁷⁰ who competitively hydrogenated benzene, toluene, and the xylenes on Raney nickel and concluded that their competitive adsorption data were independent of the nature of the solvent. These workers have studied extensively the effects of solvent upon competitive hydrogenation data.

It should be pointed out that the relative strengths of acceptor adsorption have been explained primarily on the basis of steric effects resulting from nuclear substituents. It is possible that electronic effects of the substituents may affect the ease of adsorption. The presence or absence of such effects may likely be shown by competitively

reducing acceptors which have substituents exerting upon the nucleus different effects of electron release and withdrawal (e.g., toluene and benzoic acid). Previous studies of the hydrogenation rates of the methoxybenzoic⁴⁸ and methylbenzoic⁴⁷ acids have revealed that the relative reduction rates of these compounds parallel those of the methyl, methoxy,⁴⁸ and hydroxy benzenes.⁴⁹ It thus appears that the rate-determining step itself is relatively insensitive to electronic effects of nuclear substituents.

As mentioned before, one of the most salient results of this investigation is the correspondence of the relative ease of adsorption with the relative reduction rate as nuclear substitution is increased and the lack of correspondence of these two effects for a given set of substitutional isomers. Thus, it is most logical to conceive of these effects as being separate and distinct. The ease of adsorption is a thermodynamic effect which depends upon the relative stabilities of acceptors in solution and acceptors chemisorbed on the active portion of the catalyst. The relative reduction rate, on the other hand, is a kinetic effect which mainly depends upon the relative stabilities of the transition states of the rate-determining step. An increase in nuclear substitution which decreases the stability of the chemisorbed ring by virtue of steric strain will also decrease the stability of the transition state. For a given isomeric set of polymethylbenzenes, it appears that symmetry of substitution will have opposite effects upon the stability of the chemisorbed acceptor and the transition state of the rate-determining step. It should be realized that any postulated

structure of the transition state of the slow reaction step is much more speculative than a postulated structure of the chemisorbed acceptor. The transition state will exist for a period of time of the order of a molecular vibration (c.a., 10^{-13} sec.); whereas, the chemisorbed acceptor will exist for an interval which is greater than this by several powers of ten.

It is also possible that the experimentally observed differences in the reduction rates are due to different amounts of hindrance which the nuclear substituents present toward the approach of hydrogen to the ring. If such is the case, the differences in rates do not arise from differences in transition state energy, but from differences in entropy of activation. As the hindrance to approach of hydrogen increases, the entropy of activation will decrease algebraically, and the rate will thus decrease.

The kinetics of the reaction, first order in hydrogen and zero order in acceptor, further substantiate the independence of acceptor adsorption and the rate-determining step. According to these kinetics, acceptor adsorption cannot be the slow step. Any participation of the acceptor in this step must be as a strongly adsorbed reactant on the catalyst surface. This participation will be distinctly different from the act of adsorption on the surface. Therefore, differences in the molecular structure of the acceptor may or may not affect the reduction rate in the same way as they affect the ease of adsorption.

C. Relation of This Investigation to the Hydrogenation

Mechanism of the Benzene Nucleus

The kinetic argument given in Chapter II has concluded that the rate-determining step of the reduction of the benzene nucleus on platinum may be one of the following steps:

- (1) Chemisorption of hydrogen followed by rapid surface interaction of hydrogen and acceptor;
- (2) Chemisorption of hydrogen followed by rapid attack by acceptor from the van der Waals layer;
- (3) Attack of chemisorbed acceptor by hydrogen from the van der Waals layer;
- (4) Surface interaction of chemisorbed hydrogen and chemisorbed acceptor.

The results of this work as well as their explanation suggest that the acceptor is adsorbed on the catalyst surface in an equilibrium step and then undergoes slow attack by hydrogen. This idea is compatible with either step (3) or (4) as the slow step; it does not agree with either step (1) or (2) as the slow step. It is in agreement with other experimental evidence which indicates hydrogen chemisorption on platinum to be very rapid.

Adsorption studies^{23,24} have shown that hydrogen is adsorbed with great rapidity on a clean platinum surface at room temperature. It should be remembered that the catalyst surface used in this work was definitely not a clean one. A valid measure of the lower limit of the rate of hydrogen chemisorption on platinum should be the rate of

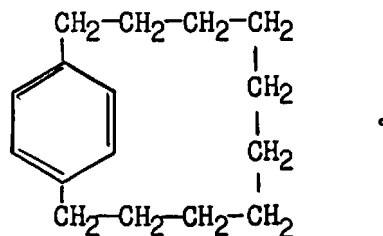
exchange of hydrogen and deuterium on this surface. The rate of hydrogen chemisorption on a platinum surface cannot be less than the exchange rate of hydrogen isotopes. The hydrogen-deuterium exchange is known to be quite rapid on platinum at temperatures as low as 78° K and hydrogen pressures of 0.1 mm. mercury.⁹⁷ It is thus reasonable to conclude that at room temperature and pressures greater than 1 atmosphere, hydrogen chemisorption is extremely rapid. This conclusion is, of course, based upon a positive temperature coefficient for the exchange. Trapnell,⁹⁸ in reviewing the hydrogen-deuterium exchange and the chemical ortho-para hydrogen conversion, has concluded that these reactions invariably have a positive temperature coefficient. A more recent investigation⁹⁹ has revealed that on platinum supported upon silica, hydrogen and deuterium are equilibrated at an extremely fast rate at room temperature.

An extenuating factor in the above argument is the inhibiting effect which olefins and aromatics exert upon the hydrogen-deuterium exchange.¹⁰⁰ The inhibition resulting from benzene is much less than that resulting from olefins. Greenhalgh and Polanyi¹⁰¹ have disclosed that benzene decreases the rate of hydrogen-deuterium exchange on platinum by approximately a factor of ten. More recent work by Smith and McDaniel¹⁰² has disclosed that a 1.125 molar solution of benzene in glacial acetic acid decreases by approximately one-half the rate of exchange between deuterium and the solvent on Adams platinum. Studies of Line, Wyatt, and Smith¹⁰³ have shown that the exchange on Adams platinum of deuterium and glacial acetic acid under the same conditions as used in this work would be approximately four orders of magnitude

greater than the reduction of benzene which was measured in this investigation. Since the rate of hydrogen chemisorption cannot be slower than the rate of this exchange, it may thus be concluded that the kinetics which were measured in this research were not determined by the rate of hydrogen chemisorption.

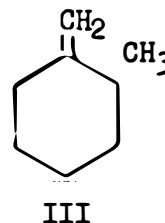
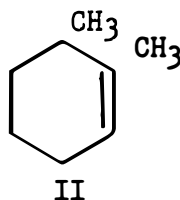
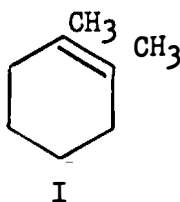
The above-mentioned exchange work verifies the presence of equilibria between hydrogen in the gaseous phase, hydrogen chemisorbed on the catalyst surface, and hydrogen in the solvent molecules. The present knowledge of the participation of the solvent molecules in the reaction mechanism is quite meager. It is likely that a significant portion of the hydrogen which is added to the ring comes originally from the solvent. Thus, as the hydrogenation reaction proceeds, it is accompanied by exchange between gaseous hydrogen, hydrogen chemisorbed on the active surface, hydrogen from the solvent molecules, and even hydrogen from the benzene nucleus itself.¹⁰⁴

It thus appears that the rate-determining step will involve the attack of the chemisorbed nucleus by hydrogen either from adjacent catalyst sites (Langmuir-Hinshelwood mechanism) or the van der Waals layer (Rideal mechanism). The former possibility is the more probable one. There is good reason to believe that a differentiation between these two mechanisms would result from systematic hydrogenation studies of compounds which have the back side of the ring blocked by a chain of atoms bridging the para positions of the ring,



This type of compound is called a paracyclophane, and its molecular geometry is such that the carbon chain lies across one face of the ring. Fortunately, many of the paracyclophanes have been synthesized and studied by Cram.¹⁰⁵

On the basis of the results reported in this thesis, there is good reason to believe that the least substituted side of the benzene nucleus accepts the first molecule of hydrogen. This conclusion is supported by the finding of Siegel and Smith,¹⁰⁶ who competitively reduced 1,2-dimethylcyclohexene (I), 2,3-dimethylcyclohexene (II), and 2-methylmethylenecyclohexane (III) over Adams platinum in glacial acetic acid,



The selective reduction of these olefins was found to decrease in the order of III, II, I; whereas, the relative reduction rates were,

$$\text{III} \approx \text{II} > \text{I} \quad .$$

If the addition of hydrogen is initiated at the least substituted portion of the ring, it follows that the last molecule of hydrogen will add to the most highly substituted portion of the ring. Hence, the

stereoisomer which is produced in the case of the xylenes will result from the addition of the last molecule of hydrogen. This conclusion has also been reached by Siegel and Dunkel,⁵³ who found that the cis-trans product ratios resulting from the reduction of the xylenes and their Δ^1 tetrahydro derivatives are quite similar. A later investigation¹⁰⁷ has shown that methyl phthalate and methyl Δ^1 -tetrahydrophthalate yield the same ratio (100 per cent cis) of stereoisomers upon reduction on Adams platinum in glacial acetic acid. Thus, there is sound reason to state that for disubstituted benzenes the addition of the first molecule of hydrogen will be rate-determining, and the addition of the last molecule of hydrogen will be product-determining. The predominance of the cis isomer in the product suggests that all of the hydrogen adds from the same side of the ring.

It should be pointed out that the idea of stepwise addition of hydrogen is in contravention to the multiplet theory of Balandin.³² However, there is a wealth of experimental evidence which justifies the concept of stepwise addition.^{49,108,109,110} With the acceptors studied in this work, it is quite unlikely that any of the dihydro or tetrahydro reduction intermediates could be isolated because they will be reduced at a much greater rate than the parent aromatic. Smith and Meriwether¹¹¹ found that on Adams platinum, cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene are reduced eight, six, and four times, respectively, more rapidly than benzene. According to the mechanism of stepwise addition of hydrogen, it is possible that the ring may become desorbed and then readsorbed between the acceptance of successive molecules of hydrogen.

As stated previously, the most likely mechanism by which the individual hydrogen molecules add to the benzene nucleus is that of Langmuir and Hinshelwood. Thus, the strongly chemisorbed ring will interact with weakly chemisorbed hydrogen. Recent studies of hydrogen chemisorption on platinum¹¹² and the infrared absorption spectra of hydrogen adsorbed on alumina supported platinum¹¹³ have shown that hydrogen is adsorbed on a platinum surface in both the atomic and molecular forms. It is quite likely that each hydrogen molecule will add to the ring as two separate hydrogen atoms (Horiuti-Polanyi mechanism) rather than simultaneously as an activated molecule. Recent stereochemical studies^{53,106,107,114} have been more compatible with this mechanism than with the one of Farkas and Farkas.⁶⁰ The Horiuti-Polanyi mechanism also appears to provide a more valid explanation of the exchange between deuterium and benzene on platinum than does the Farkas and Farkas mechanism.¹¹⁵ If the Horiuti-Polanyi mechanism is operating for the reduction of the benzene nucleus on platinum at room temperature, the reaction kinetics dictate that the rate-determining step will be the addition of the second atom of hydrogen to the ring.

CHAPTER VI

SUMMARY

The competitive catalytic hydrogenation of benzene, toluene, and the polymethylbenzenes has been studied on platinum at 30° and hydrogen pressures of 3-5 atmospheres. Glacial acetic acid was used as solvent. The kinetics of the reduction of each of these hydrocarbons have also been investigated.

For all of the compounds studied, the reaction kinetics were found to be first order in hydrogen pressure and zero order in the concentration of hydrogen acceptor under conditions where the experimental rate was independent of diffusion processes. The reduction rate was found to decrease with increasing nuclear substitution and increase with symmetry of substitution. These results agree satisfactorily with previous kinetic studies.

The competitive hydrogenations were carried out with various binary mixtures of acceptors, and the data from these reductions were treated mathematically with a method based on Langmuir kinetics. This treatment yielded a quantitative measure of the relative ease of adsorption of the various acceptors on the active portion of the catalyst surface. It was found that the ease of adsorption decreased with increasing nuclear substitution except in the case of hexamethylbenzene, which was slightly more easily adsorbed than pentamethylbenzene. For a given set of substitutional isomers, the ease of adsorption decreased with increasing symmetry of substitution. Hence, the ease of adsorption on

the active surface did not necessarily parallel the relative reduction rate.

The relative ease of adsorption of the various acceptors has been explained on the basis of six-point attachment of the benzene ring to the active surface. The relative amounts of steric strain resulting from this mode of adsorption and the opportunity for inclined adsorption of the ring with respect to the catalyst surface permit a ready rationalization of the experimental facts. The abnormally high relative ease of adsorption of hexamethylbenzene is explained as being the result of a solvent-affinity effect. An argument is presented which concludes that the rate-determining step in the hydrogenation of the benzene nucleus on platinum is the attack of the strongly adsorbed nucleus by hydrogen either from adjacent catalyst sites or from the van der Waals layer.

The analysis of the reaction mixtures from the competitive reductions required the development of an analytical method for the determination of binary mixtures of benzene, toluene, and the polymethylbenzenes in glacial acetic acid. This method is based on ultraviolet absorption spectrophotometry and is capable of an accuracy of ± 3 per cent.

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